Fruit peels as sources of non-extractable polyphenols or macromolecular antioxidants: analysis and nutritional implications

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Abstract

Despite increasing interest in the relevance of non-extractable polyphenols (NEPP) or macromolecular antioxidants as food bioactive compounds, most studies on their presence in foods focus mainly on the edible part of specific fruits, but their potential presence in fruit peels is usually ignored. The aim of this study was to evaluate NEPP content in the peels from ten common fruits. The results showed that NEPP made up more than half of the total polyphenol contents in half of the studied samples. HPLC analysis showed that NEPP were constituted by phenolic acids, flavanols and flavonols. Also, it was found that peels accounted for more than 40% of total NEPP in the fruit in four of the samples analysed. These results should encourage both the use of fruit peels in the fruit industry as ingredients and the consumption of whole fruits given the significant presence of NEPP in fruit peels.

Keywords: fruit peels; non-extractable polyphenols; macromolecular antioxidants; hydrolyzable polyphenols; non-extractable proanthocyanidins; food byproducts.
Abbreviations

EPP: extractable polyphenols.
HBA: hydroxybenzoic acids.
HCA: hydroxycinnamic acids.
HPP: hydrolyzable polyphenols
MACAN: macromolecular antioxidants.
NEPA: non-extractable proanthocyanidins.
NEPP: non-extractable polyphenols.
1. Introduction

During the last two decades non-extractable polyphenols (NEPP) have emerged as important contributors to total polyphenol content in plant foods (Bravo, Abia, & Saura-Calixto, 1994; Pérez-Jiménez, Díaz-Rubio, & Saura-Calixto, 2013; Saura-Calixto & Pérez-Jiménez, 2018). Their name is derived from the fact that, during the aqueous-organic treatments commonly performed to evaluate polyphenol content in foods, they are not extracted, thus remaining in the discarded residues. This is due to the chemical nature of this fraction of dietary polyphenols, since NEPP include both high molecular weight polyphenols such as non-extractable proanthocyanidins (NEPA) and low molecular weight polyphenols associated with macromolecules (proteins, dietary fibre), in this case hydrolyzable polyphenols (HPP); in view of this, an equivalent term has become current, most recently macromolecular antioxidants (MACAN) (Pérez-Jiménez & Saura Calixto, 2015). Besides analytical reasons explaining why this fraction of food bioactive compounds has been ignored for decades, the point is that they make a major contribution to total polyphenol intake (Arranz, Silván, & Saura-Calixto, 2010; Saura-Calixto & Pérez-Jiménez, 2018) and there is promising evidence of their health-related properties (Pérez-Jiménez et al., 2013).

Nevertheless, data on NEPP content in foods are still limited. It is important to augment this information in order to develop databases focused on NEPP, to better estimate NEPP intake in different populations or to identify the richest dietary sources of NEPP so as to perform specific clinical trials. In this respect, fruits have been shown to be significant sources of NEPP, and several studies have reported NEPP content in the most widely-consumed fruits in Europe (Pérez-Jiménez & Saura Calixto, 2015) or in some tropical fruits (Rufino et al., 2011; Rufino et al., 2010). At the same time, several plant materials
commonly discarded during food processing have been shown to be particularly rich
sources of NEPP—for instance grape or pomegranate pomaces (Pérez-Jiménez, Arranz, &
Saura-Calixto, 2009; Pérez-Ramírez, Reynoso-Camacho, Saura-Calixto, & Pérez-Jiménez,
2018). Their identification as sources of bioactive compounds may offer new functions for
these materials, which are currently used only for low added value activities.
Common fruits generate large amounts of discarded peels, both when consumed in the
home and when industrially transformed to produce juices, jams or other derived products.
These materials are known to be of nutritional value due to their high dietary fibre content
(Jiménez-Escrig, Rincón, Pulido, & Saura-Calixto, 2001); however, NEPP content has only
been evaluated for some specific fruits, such as mango or pineapple (Larrauri, Rupérez, &
Saura Calixto, 1997; Safdar, Kausar, & Nadeem, 2017).
Therefore, the starting hypothesis of this study was that peels from common fruits contain
relevant amounts of NEPP. In order to test this, we performed a comparative evaluation of
NEPP content in peels from a selection of common fruits, and to estimate their contribution
to total polyphenol content.

2. Materials and Methods

2.1 Samples

The following samples were acquired in local supermarkets: apple (var. Fuji from Italy,
Golden from Italy and Granny Smith from France), banana (Del Monte, from Colombia),
kiwi (var. Hayward, from Portugal), mandarin (var. Tang Gold from Spain), mango (var.
Osteen from Spain), melon (var. Piel de sapo or Santa Claus from Spain), nectarine (var.
Venus from Chile), orange (var. Newhall, from Spain), pear (var. Blanquilla from Spain)
and watermelon (var. Imperial from Spain). Peels were removed taking as less as possible
amount of pulp; then, peel and pulp were weighed in order to get the proportion of each
fraction. Peels were later freeze-dried and milled in a centrifugal mill (Retsch ZM 200, Haan, Germany) to a particle size of 0.5 mm. Peels from three independent fruits were mixed to get a representative sample of each fruit item.

2.2 Reagents

Gallic acid and hydrochloric acid were from Sigma-Aldrich (St. Louis, MO, USA). The Folin–Ciocalteu reagent was from Panreac, Castellar del Vallés, Barcelona, Spain. All the reagents used were of analytical or HPLC grade, depending on the analysis.

Condensed tannin concentrate from Mediterranean carob pods (*Ceratonia siliqua* L) was supplied by Nestlé Ltd. (Vers-chez-les Blancs, Switzerland).

2.3 Preparation of polyphenol fractions

Polyphenol fractions were obtained as previously described (Arranz, Saura-Calixto, Shaha, & Kroon, 2009):

*Extractable polyphenols*. Briefly, 0.5 g of sample was placed in a capped centrifuge tube, 20 mL of acidic methanol/water/HCl (50:50, v/v; pH 2) was added and the tube was thoroughly shaken at room temperature for 1 h. The tube was centrifuged at 2,500 g in a Thermo Heraeus Megafuge 11 (Thermo Fisher, Waltham, MA, USA) for 10 min and the supernatant was recovered. Twenty millilitres of acetone/water (70:30, v/v) was added to the residue, and the shaking and centrifugation were repeated. The methanolic and acetonic extracts were combined, corresponding to EPP solutions.

*NEPP-Hydrolyzable polyphenols (HPP)*. Three residues from EPP extractions were subjected to hydrolysis with methanol and sulphuric acid for 20 h at 85°C (Hartzfeld, Forkner, Hunter, & Hagerman, 2002) and the pH was later adjusted to 5.5. These hydrolysates were then subjected to SPE treatment with Oasis HLB cartridges (5400 mg, 3cc, 30 µm) from Waters (Milford, MA, USA) in order to remove salts that may have
damaged chromatographic columns: after activation with methanol (5 mL) and methanol 50% (5 mL), 1 mL of the sample was loaded and it was eluted successively with methanol (1 mL) and methanol 80% (1 mL). The eluates were combined and concentrated under nitrogen.

**NEPP-Non extractable proanthocyanidins (NEPA).** Three residues of EPP extraction were treated with butanol/HCl/FeCl₃ at 100ºC for 1 h (Pérez-Jiménez et al., 2009; Porter, Hrstich, & Chan, 1985).

### 2.3 Analysis of polyphenols fractions

Total polyphenol content correspond to the sum of EPP, HPP and NEPA. While EPP and HPP may be determined either spectrophotometrically -providing the content of each polyphenol fraction- or by HPLC -providing polyphenol profile-, NEPA can only be estimated by spectrophotometric determination.

#### 2.3.1 Polyphenol fractions

EPP and HPP content were determined in the solutions described above according to the Folin-Ciocalteu method (Singleton, Orthofer, & Lamuela-Raventós, 1998). A test sample (0.5 mL) was mixed with 1 mL of Folin-Ciocalteu reagent and swirled. After 3 min, 10 mL of sodium carbonate solution (75 g/L) was added and mixed. Additional distilled water was mixed in thoroughly by inverting the tubes several times. After 1 h, the absorbance at 750 nm was recorded. The results were expressed as mg/100 g gallic acid equivalents (GAE).

NEPA content in the solution obtained by depolymerization by butanolysis was measured at 555 and 450 nm (Zurita, Díaz-Rubio, & Saura-Calixto, 2012) in order to detect anthocyanins and xanthylium compounds, respectively. The results were compared with a carob pod (*Ceratonia siliqua*) proanthocyanidin standard, which is rich in high molecular weight proanthocyanidins.
2.3.2 Polyphenol profile

Polyphenol classes were measured by HPLC-DAD in the EPP and HPP solutions described above, based on methodologies previously described (Pérez-Jiménez & Saura Calixto, 2015). Briefly, an Agilent 1200 series LC (Santa Clara, CA, USA) was used. A 20 µL sample was separated in a chromatography column with the following characteristics: Luna C18 (50 x 2.1 mm i.d.) 3.5-µm particle with Phenomenex Securityguard C18 (4 x 3 mm i.d.) column (Torrance, CA, USA). Gradient elution was performed with a binary system consisting of [A] 0.1% aqueous formic acid and [B] 0.1% formic acid in acetonitrile. The following increasing linear gradient (v/v) of [B] was used (t, %B): (0, 6), (10, 23), (15, 50), (20, 50), (23, 100), (25, 100), (27, 8) and (30, 8), followed by a re-equilibration step. The flow was set at 0.4 mL/min. Signals were collected at the maximum wavelengths reported for the different polyphenol classes: 214 nm (flavanols), 280 nm (hydroxybenzoic acids and flavanones), 320 nm (hydroxycinnamic acids), 365 nm (flavonols) and 520 nm (anthocyanins). The results were expressed as equivalents of the appropriate standards for each polyphenol class (calibration curves, 1-20 ppm): vanillic acid for hydroxybenzoic acids (y= 19.003x + 14.145, R²= 0.9953); ferulic acid for hydroxycinnamic acids (y= 28.192x + 1.879, R²= 0.9957); (-)-epicatechin for flavanols (y= 32.346x + 14.892, R²= 0.9971); naringenin for flavanones (y= 15.894x + 6.081, R²= 0.9973); and rutin for flavonols (y= 2.985x + 0.389, R²= 0.9987). Anthocyanins were not detected in any of the samples, so calibration curves were not needed for these polyphenol classes. When different classes shared a maximum wavelength, the complete UV-spectrum was evaluated to ascertain to which class the peak corresponded.

2.4 Statistical analysis
Data are shown as mean ± standard deviation. Since results did not exhibit normal
distribution (assessed by Shapiro-Wilk test), the non-parametric Kruskal-Wallis $H$ test,
followed by Mann-Whitney $U$ test were applied to determine the existence of significant
differences ($p < 0.05$) between the samples. Data were analysed with the statistical SPSS
IBM 24 package for Windows.

3. Results

3.1 Total EPP and NEPP contents in fruit peels

Table 1 shows total EPP and NEPP contents in peels from common fruits. EPP contents
ranged between 305.3 mg/100 g dw in watermelon to 4,224.7 mg/100 g dw in mango ($p <
0.05$). As for NEPP, HPP were detected in all samples, while NEPA were present only in
half of them (apple, banana, kiwi, nectarine and pear). HPP ranged from 271.9 mg/100 g
dw in nectarine to 1,945.4 mg/100 g dw in banana ($p < 0.05$). The range of variation of
NEPA was wider, moving from 2564.4 mg/100 g dw in pear to 7,667.2 mg/100 g dw in
banana ($p < 0.05$).

But the most significant factor is the contribution of NEPP to total polyphenol content in
these samples. As shown in Table 1, this contribution ranged from 7% in mango to 82% in
banana. Indeed, in half of the studied samples NEPP made up more than half of the total
polyphenol content.

3.2 Profile of EPPs and NEPPs in fruit peels

A detailed HPLC analysis was performed in the EPP and HPP fractions—as explained
above, this was not possible in the NEPA fraction. Of EPP, the following polyphenol
classes were identified (the richest samples for each class are shown in parentheses):
hydroxycinnamic acids (mandarin, melon), flavanols (orange, mango, mandarin), flavonols
(pear, melon, banana), flavanones (mandarin). In the case of HPP, flavanones were not
detected and flavonols were only found in mango. Hydroxycinnamic acids (the highest contents were found in melon, orange and pear) and flavanols (especially in melon and pear) were also detected in HPPs. Additionally, hydroxybenzoic acids (mainly in melon and mango) were detected in this polyphenol fraction.

3.3 Contribution of fruit peels to NEPP content in whole fruits

In order to arrive at an estimation of the contribution of NEPP to total NEPP content in fruits (considering both peel and pulp), previously published data on NEPP content in the pulps of the fruits analysed here (except mango and kiwi) were integrated with those from the present study. It was found (Table 3) that peels made up more than 40% of total NEPPs in four of the samples analysed (in ascending order: nectarine, orange, watermelon and mandarin).

Therefore, considering the total NEPP content in fruit peels (Tables 1-2) and the relative contribution of peels to total NEPP content in fruits (Table 3), discarding peels from common fruits has nutritional and technological implications, as discussed below.

4. Discussion

In this study we explored polyphenol content in fruit peels, a significant part of plant foods commonly discarded in both domestic and industrial processing. Significant concentrations of EPP were found in the peels of common fruits; they agreed with previously reported data for some of the samples analysed here, such as mango (Safdar et al., 2017) or orange (Lagha-Benamrouche & Madani, 2013). Interestingly, EPP content in the peels of most of the samples were in the same range as previously reported EPP content in their pulps; for instance, EPP contents for apple and pear peels registered here were 1,278 and 721 mg/100 g dw respectively, while mean reported values for the pulps of the two fruits were 1,707 and 540 mg/100 g dw (Pérez-Jiménez, Neveu, Vos, & Scalbert, 2010).
Nevertheless, the main purpose of this study was to ascertain the presence of NEPP or macromolecular antioxidants in fruit peels, since the starting hypothesis was that fruit peels contain relevant amounts of these compounds. Despite increasing interest in the relevance of NEPP as food bioactive compounds, most of the studies on their presence in foods focus on specific food items (Gonzales et al., 2015; White, Howard, & Prior, 2010), and categorized lists of foods are still scarce (Hellström & Mattila, 2008; Pérez-Jiménez & Saura Calixto, 2015). It is therefore of interest to achieve a comprehensive overview of the presence of NEPP in fruits so as to produce data for the development of databases or to estimate dietary intakes. Moreover, the simultaneous study of EPP and NEPP using the same methodology in a wide number of samples makes it possible to directly compare the results and to determine the relative contribution of NEPP to total polyphenol content. Finally, in the particular case of fruit peels there is an interest in the study of NEPP as a potential reason for the revalorization of these byproducts. The results reported here for total EPP and NEPP contents (determined as their main classes, HPP and NEPA) show that NEPP are significant bioactive compounds in fruit peels, and indeed are present in many common fruits in even higher proportions than EPP. However, the NEPP fraction of food bioactive compounds has not been considered in most previous characterizations of fruit peels (Brahem et al., 2017; Lagha-Benamrouche & Madani, 2013).

Another important goal in the search for more knowledge about NEPP is not only to know their total content, but also their detailed composition. This is relevant because certain health-related properties of polyphenols may be specifically ascribed to some classes, such as the recognized effects of flavanols on endothelial function (EFSA Panel on Dietetic Products, 2012). HPLC data on the different polyphenol classes were therefore recorded for both EPP and NEPP.
The results for EPP agreed with some previous data for certain fruit peels such as pear, where the most abundant phenolic compounds are flavonols, with much lower concentrations of phenolic acids and monomeric flavanols (Brahem et al., 2017). Nevertheless, the most abundant polyphenols in pear peels are proanthocyanidins, which cannot be determined by reverse phase HPLC. This also affects the samples analysed here and the data would be especially relevant for those known to have significant proanthocyanidin concentrations in the pulp, e.g. apple, since large amounts of these may also be expected in the peel.

In the case of NEPP it is interesting to note that, as shown in previous studies (Arranz et al., 2010) and also found here, these are composed not only of phenolic acids—as initially considered for the particular case of HPP in cereals—but also of flavanols and flavonols. Nevertheless, the flavonoid content in NEPP exceeded that of phenolic acids only in banana. A previous study (Ajila & Prasada Rao, 2013) characterized the non-extractable phenolic acid profile in mango peel, identifying gallic acid, protocatechuic acid, syringic acid and ferulic acid; interestingly, the major compound was gallic acid, which agrees with our finding that the non-extractable hydroxybenzoic acid content (117.6 mg/100 g dw) was much higher than the hydroxycinnamic acid content (29.6 mg/100 g dw). As in the case of proanthocyanidins in the EPP fraction, due to the limitations of reverse phase HPLC for the analysis of these compounds, HPLC analysis of NEPP did not include NEPA, concentrations of which should be added to the HPLC values to obtain total NEPP content. Overall, the HPLC analysis of the samples, like the spectrophotometric determinations, showed that NEPP made a significant contribution to total polyphenol content in the samples (even considering that polymeric proanthocyanidins could not be included in these
determinations). For instance, 64% of phenolic acids in apple peel were present as NEPPs, which agrees with other recent findings (Lee, Chan, & Mitchell, 2017).

Additionally, the contribution of peel to total NEPP content in the whole fruit was determined, showing that in some samples NEPP in peel accounted for more than 40% of total NEPP in the fruit. Overall, the data recorded here on the presence of NEPP in fruit peels have technological and nutritional implications. For fruits with non-edible peels (such as melon or banana), this significant NEPP content should be seen as an added reason (together with their EPP content and their known dietary fibre content) to use these materials, commonly discarded in food the industry, as ingredients in new foods. In particular, they could be used either as antioxidant additives or as functional ingredients. For instance, another food byproduct rich in NEPP, grape pomace, has already been explored for its applications as a food ingredient in different matrixes for animal feeding (Brenes, Viveros, Chamorro, & Arija, 2016; García-Lomillo & González-SanJosé, 2017; Solari-Godiño, Pérez-Jiménez, Saura-Calixto, Borderías, & Moreno, 2017). Interestingly, grape pomace also contains high concentrations of dietary fibre, which has been reported to improve the physicochemical properties of the final products (Solari-Godiño et al., 2017); this might be also the case if fruit peels were used for the same purpose. In particular, some preliminary studies have explored the use of fruit peels as ingredients, such as banana peel in cereal bars (Carvalho & Conti-Silva, 2018) or mango peel and orange peel in biscuits (Ajila, Leelavathi, & Prasada Rao, 2008; Obafaye & Omoba, 2018); in all cases, the products exhibited good sensory properties, indicating the potential for the use of these by-products. Besides, the high presence of NEPP in these materials could be useful for their application in active packaging, as it has been done with extractable polyphenols obtained from apple peel (Riaz et al., 2018).
Also, the results obtained here have nutritional implications in terms of general recommendations. NEPP have been reported to exhibit some specific advantages as compared with EPP that may affect their health-related properties. In particular, longer colonic transformation times have been reported, promoting a sustained circulation of beneficial metabolites (González-Sarrías, Espín, & Tomás-Barberán, 2017). Also, given their strong association with dietary fibre, they affect the colonic fermentation of the fibre and vice versa (Saura-Calixto et al., 2010). Therefore, joint consumption of EPP and NEPP may produce complementary beneficial effects (Pérez-Jiménez et al., 2013). Thus, considering the significant proportion of NEPP in fruit peels, the NEPP content of fruits that can be consumed with peel would be an additional reason to promote the consumption of whole fruits, along with the EPP and dietary fibre contents already mentioned. For instance, a serving of apple and pear consumed with peel would mean additional intakes of 82 and 58 mg of NEPPs respectively. This would lead to a substantial increase in current NEPP intake from fruits, which has been estimated for different European countries in the range of 300–400 mg/p/day (Pérez-Jiménez & Saura Calixto, 2015). Such a recommendation would ensure a higher intake of NEPPs, always subject to doses that can realistically be achieved through diet.

Nevertheless, some aspects should be considered before a high-scale promotion of fruit peels, in particular from those that have been discarded up to the moment. Regarding the nutritional composition, the potential presence of antinutrients should be evaluated. Anyway, levels of heavy metals, oxalates, saponines and cyanogen glucosides were evaluated in banana peels, concluding that their concentrations did not constitute a health hazard (Adebayo Adeniji, Samuel Barimalaa, Tenkouano, Oladimeji Sanni, & Hart, 2008); similar levels could be expected in other fruit peels. Similarly, potential allergens should be
evaluated, since they are widely known, for instance, in peach peel. Finally, the presence of pesticide residues should be assessed. Industrial and homemade washing procedures have shown to be able to significantly decrease the levels of some pesticides, although they are not so effective for others (Li et al., 2012; Yang et al., 2017), so each specific case should be considered. This could be particularly relevant for banana peel, which was signalled as the food item with the highest prevalence of multiple residues in the 2015 European Union report on pesticide residues in food (EFSA, 2017).

In summary, this study evaluated total polyphenol content, considering both EPP and NEPP in peels from common fruits. The results showed that these plant materials, commonly discarded in both domestic and industrial processing, are rich sources of polyphenols. In particular NEPP, which have been less studied, may account for more than 50% of total polyphenols in fruit peels. These results should encourage both the use of fruit peels in the fruit industry as ingredients and the consumption of whole fruits, given the significant presence of NEPP in fruit peels.

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Competing interests
There are no conflicts to declare.

Contributors
F.S.-C. conceived the research, J.P.-J. performed the research, analysed the data and wrote the first draft of the manuscript. All authors approved the final article.

References


TABLE LEGENDS

Table 1. Polyphenol content (mg/100 g dw) in peels from common fruits.
Spectrophotometric determinations.

Table 2. Polyphenol profile by HPLC-DAD (mg/100 g dw) in peels from common fruits.

Table 3. Contribution of fruit peels to NEPP content in whole fruits
Table 1. Polyphenol content (mg/100 g dw) in peels from common fruits. Spectrophotometric determinations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>EPP</th>
<th>NEPP</th>
<th>NEPP contribution to total polyphenol content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple</td>
<td>1278.7 ± 45.1a</td>
<td>263.3 ± 31.4a</td>
<td>32</td>
</tr>
<tr>
<td>Banana</td>
<td>2,116.7 ± 112.1b</td>
<td>1,961.3 ± 175.6b</td>
<td>82</td>
</tr>
<tr>
<td>Kiwi</td>
<td>1,522.0 ± 23.2c</td>
<td>658.6 ± 39.4c</td>
<td>79</td>
</tr>
<tr>
<td>Mandarin</td>
<td>2,184.3 ± 41.8b</td>
<td>655.3 ± 44.3c</td>
<td>23</td>
</tr>
<tr>
<td>Mango</td>
<td>4,224.7 ± 173.5d</td>
<td>323.7 ± 24.4a</td>
<td>7</td>
</tr>
<tr>
<td>Melon</td>
<td>316.2 ± 30.2e</td>
<td>651.8 ± 48.7c</td>
<td>67</td>
</tr>
<tr>
<td>Nectarine</td>
<td>1,797.5 ± 15.7f</td>
<td>338.7 ± 57.4a</td>
<td>25</td>
</tr>
<tr>
<td>Orange</td>
<td>1,894.5 ± 180.3f</td>
<td>466.8 ± 57.3d</td>
<td>80</td>
</tr>
<tr>
<td>Pear</td>
<td>721.1 ± 34.8g</td>
<td>1,411.8 ± 111.9e</td>
<td>70</td>
</tr>
<tr>
<td>Watermelon</td>
<td>305.3 ± 28.8e</td>
<td>520.6 ± 47.1f</td>
<td>63</td>
</tr>
</tbody>
</table>

EPP, extractable polyphenols; HPP, hydrolyzable polyphenols; NEPA, non-extractable proanthocyanidins; NEPP, non-extractable polyphenols. n.d., non-detected. Different superscript letters indicate significant differences ($p < 0.05$).
Table 2. Polyphenol profile by HPLC-DAD (mg/100 g dw) in peels from common fruits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HCA</th>
<th>Flavanols</th>
<th>Flavonols</th>
<th>Total</th>
<th>HBA</th>
<th>HCA</th>
<th>Flavanols</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple</td>
<td>46.9 + 5.4a</td>
<td>188.0 + 1.4a</td>
<td>n.d.a</td>
<td>234.9 + 5.6a</td>
<td>n.d.a</td>
<td>26.4 + 7.6a</td>
<td>8.0 ± 0.6a</td>
<td>34.4 ± 7.7a</td>
</tr>
<tr>
<td>Banana</td>
<td>3.5 ± 0.3b</td>
<td>n.d.b</td>
<td>98.9 ± 3.5b</td>
<td>102.4 ± 3.5b</td>
<td>0.4 ± 0.1b</td>
<td>n.d.b</td>
<td>15.0 ± 0.4b</td>
<td>15.4 ± 0.4b</td>
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<tr>
<td>Kiwi</td>
<td>3.8 ± 0.3b</td>
<td>n.d.b</td>
<td>97.6 ± 2.0c</td>
<td>13.6 ± 0.2c</td>
<td>94.5 ± 2.0c</td>
<td>n.d.a</td>
<td>31.8 ± 6.8c</td>
<td>0.9 ± 0.2c</td>
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<tr>
<td>Mandarin</td>
<td>380.7 ± 12.2c</td>
<td>459.7 ± 5.3d</td>
<td>n.d.a</td>
<td>1,079.2 ± 13.4d</td>
<td>n.d.a</td>
<td>66.6 ± 7.6d</td>
<td>14.2 ± 1.4bd</td>
<td>80.8 ± 7.7c</td>
</tr>
<tr>
<td>Mango</td>
<td>n.d.d</td>
<td>466.5 + 4.2d</td>
<td>n.d.a</td>
<td>466.5 ± 4.2d</td>
<td>117.6 ± 5.6c</td>
<td>29.6 ± 3.6ace</td>
<td>10.8 ± 1.3c</td>
<td>164.0 ± 6.8d</td>
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<td>Melon</td>
<td>16.8 ± 0.8e</td>
<td>109.7 ± 1.3e</td>
<td>103.4 ± 2.6d</td>
<td>229.9 ± 3.0f</td>
<td>511.4 ± 189.2d</td>
<td>151.6 ± 28.7c</td>
<td>96.2 ± 14.1f</td>
<td>759.3 ± 191.9e</td>
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<td>Nectarine</td>
<td>388.9 ± 15.7c</td>
<td>86.0 ± 3.1f</td>
<td>26.1 ± 1.2e</td>
<td>501.1 ± 16.0g</td>
<td>n.d.a</td>
<td>69.9 ± 5.9d</td>
<td>6.6 ± 0.7g</td>
<td>76.5 ± 5.9c</td>
</tr>
<tr>
<td>Orange</td>
<td>44.0 ± 4.5a</td>
<td>1,481.7 ± 71.0f</td>
<td>n.d.a</td>
<td>1,525.7 ± 71.0b</td>
<td>n.d.a</td>
<td>107.7 ± 15.5f</td>
<td>9.8 ± 3.9ace</td>
<td>117.5 ± 16.0f</td>
</tr>
<tr>
<td>Pear</td>
<td>36.1 ± 2.9f</td>
<td>41.8 ± 2.5h</td>
<td>350.2 ± 2.9f</td>
<td>428.1 ± 4.9f</td>
<td>n.d.a</td>
<td>108.0 ± 1.5f</td>
<td>45.0 ± 2.1b</td>
<td>153.0 ± 2.6g</td>
</tr>
<tr>
<td>Watermelon</td>
<td>17.9 ± 1.1e</td>
<td>n.d.b</td>
<td>21.5 ± 0.7g</td>
<td>39.4 ± 1.3j</td>
<td>71.8 ± 24.5c</td>
<td>48.7 ± 13.0g</td>
<td>12.0 ± 2.0dce</td>
<td>132.2 ± 27.8f</td>
</tr>
</tbody>
</table>

HBA were not detected in the EPP fraction. Flavanones were only detected in the EPP fraction of mandarin (233.8 ± 1.6 mg/100 g dw), while flavonols were only detected in the HPP fraction of mango (5.9 ± 0.6); these values were included in the calculations of total EPP and total HPP.

EPP, extractable polyphenols; HBA, hydroxybenzoic acids; HCA, hydroxycinnamic acids; HPP, hydrolyzable polyphenols. n.d., non-detected. Different superscript letters indicate significant differences (p<0.05).
Table 3. Contribution of fruit peels to NEPP content in whole fruits

<table>
<thead>
<tr>
<th>Sample</th>
<th>NEPP content in pulp (mg/100 g fw)</th>
<th>NEPP content in peel (mg/100 g fw)</th>
<th>Peel contribution to whole fruit (% fm)</th>
<th>NEPP contribution to total polyphenols in whole fruit (% fm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple</td>
<td>249.9 ± 8.8</td>
<td>244.2 ± 8.6</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Banana</td>
<td>891.6 ± 54.2</td>
<td>258.2 ± 13.7</td>
<td>32</td>
<td>12</td>
</tr>
<tr>
<td>Mandarin</td>
<td>98.2 ± 4.6</td>
<td>653.1 ± 12.5</td>
<td>30</td>
<td>74</td>
</tr>
<tr>
<td>Melon</td>
<td>48.6 ± 2.6</td>
<td>22.5 ± 2.1</td>
<td>35</td>
<td>20</td>
</tr>
<tr>
<td>Nectarine</td>
<td>164.2 ± 8.2</td>
<td>349.5 ± 6.9</td>
<td>25</td>
<td>41</td>
</tr>
<tr>
<td>Orange</td>
<td>217.9 ± 10.3</td>
<td>441.4 ± 42.0</td>
<td>30</td>
<td>46</td>
</tr>
<tr>
<td>Pear</td>
<td>295.1 ± 7.5</td>
<td>174.5 ± 8.4</td>
<td>25</td>
<td>16</td>
</tr>
<tr>
<td>Watermelon</td>
<td>7.8 ± 1.6</td>
<td>19.2 ± 1.8</td>
<td>35</td>
<td>57</td>
</tr>
</tbody>
</table>

1 Pérez-Jiménez & Saura-Calixto, 2015. This study did not include either kiwi or mango.

NEPP, non-extractable polyphenols. NEPP values calculated as sum of hydrolysable polyphenols and non-extractable proanthocyanidins, both determined by spectrophotometric determinations.