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Valorisation of Clementine, Mandarin, and Orange Peel By-Products as Value-Added Sources of Macronutrients, Fatty Acids, and Multiple Elements

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Abstract

Clementine, mandarin, and orange peels, which are usually discarded, can serve as promising, sustainable dietary supplements with beneficial compositions, as demonstrated in this study. Citrus peels are low in ash, fat, and protein, but high in moisture, fibre, sugar, and polyunsaturated fatty acids (PUFAs) (up to 60%). They contain high levels of omega-3 and omega-6 fatty acids, up to 30% each, making them a good health-promoting source, as shown by the values of nutritional indices as follows: PUFA/saturated fatty acid (SFA) (1.94 to 2.30), monounsaturated fatty acid (MUFA)/SFA (0.39 to 0.84), and PUFA/MUFA (2.37 to 5.82). Essential macro elements (K > Ca > Mg > S > P > Na) and trace elements (Fe > Zn > Mn > Cu > Cr > Mo > Co > Se) are unevenly distributed among the peels, along with non-essential elements, with Al (37 to 51 mg/kg) and Sr (17 to 30 mg/kg) predominating. Rare elements in food, such as V and W, are found up to 41 and 79 µg/kg respectively, followed by Nb > Ga > Y > Ge (5 to 11 µg/kg). Although citrus peels have a nutrient-dense composition, their monitoring must be ensured before inclusion in the common diet, particularly regarding non-essential elements, as for most of them the reference doses are not established and they could be harmful to human health.

Keywords: citrus peel; macronutrient; fatty acid profile; nutritional indices; multi-element analysis; GC-FID analysis; ICP-MS analysis

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1. Introduction

The citrus fruits, with the scientific name *Citrus* L., belong to the *Rutaceae* family and are among the most widely cultivated crops worldwide. Their annual global production amounts to 150 million metric tonnes [1]. The best-known citrus varieties for commercial production and use include *Citrus sinensis* (sweet orange), *Citrus sinensis* L. Osbeck (blood orange), *Citrus aurantium* (sour orange), *Citrus reticulata* (mandarin), *Citrus clementina* (clementine), *Citrus limon* (lemon), *Citrus paradisi* (grapefruit), *Citrus grandis* (pummelo), *Citrus aurantifolia* (lime), *Citrus medica* (citron), and *Citrus japonica* (kumquat) [2,3]. All have similar anatomy, consisting of the following three main parts: the pulp with juice sacs, the seeds, and the peel, which is divided into the epicarp or flavedo (coloured outer layer) and the mesocarp or albedo (white, soft middle layer) [4,5]. Each citrus fruit variety and each of its parts has a different colour and organoleptic characteristics, such as

sweetness, bitterness, and astringency, which significantly influence consumer perception and use. In addition to their attractive colour, flavour, aroma, and ease of consumption, citrus fruits play an important role in human health due to their excellent nutritional and phytochemical composition.

Various studies [2,3,6,7] have shown that citrus fruits contain phytochemicals, including volatile compounds in essential oils and bioactive compounds, which are mainly localised in the peel (flavedo) and seeds [5,8]. Citrus fruits, especially the peel, are rich in phenolic acids, flavonoids, pigments (lutein, zeaxanthin, β-cryptoxanthin, β-carotene, and chlorophyll a and b), alkaloids, coumarins, and limonoids (essential oils) [2,3,5–10]. In addition to these phytochemicals, citrus peels are an excellent source of pectin, cellulose, hemicellulose, lignin, and dietary fibre contained in the albedo [2,5,8]. Citrus fruits also contain various macro- and micronutrients such as sugars, lipids and fatty acids, minerals, and vitamins [2,3,6]. Due to their excellent phytochemical and nutritional composition, citrus fruits have antidiabetic, anticancer, antioxidant, antibacterial, antifungal, antiparasitic, antiviral, hypocholesterolaemic, anti-inflammatory, antitumour, anti-obesity, and osteoprotective effects [2,6,7,11–13].

Given their beneficial role in human nutrition, the consumption of citrus fruits is steadily increasing, with fresh fruit pulp being among the most popular forms. In addition to beverages such as juice and wine, the pulp of citrus fruits is also used in preserved products (jam and marmalade) and in dried form [2,3,6,14]. Besides the pulp, citrus peels are utilised in the food industry as functional ingredients, additives, and flavourings in the production of candied products, sauces, jams, jellies, and similar items [2,6,15,16]. Beyond the food industry, peels are also used for the production of biodegradable packaging and in the pharmaceutical and cosmetics industries [5,6,17]. Not only peels, but also other solid and semi-solid fractions such as seeds and pomace, which are typically considered waste, can be used as biofertilisers and bioadsorbents [5], or alternatively as compost or animal feed [12,18,19].

Due to the valuable components of citrus by-products and the growing interest in their valorisation, several studies have suggested their beneficial use in the production of functional foods and nutraceuticals to minimise the environmental damage caused by improper waste disposal. Among citrus fruit wastes, the peel constitutes the largest proportion (about 50% of the total fruit mass) compared to other fractions such as seeds, pomace, and wastewater. The peel fractions resulting from juice production of the three most commonly consumed citrus species—sweet oranges, mandarins, and clementines—are therefore the focus of this study.

Although numerous scientific studies have demonstrated the use of citrus fruit waste mainly as a source of phytochemicals, this study presents the sustainable use of peel as a source of macronutrients, fatty acids, and multiple elements, which, to our knowledge, have not been reported in the literature for clementine, mandarin, and orange peel, nor for other citrus peel varieties.

The main contribution of this work is that it provides: (i) the macronutrient composition of the three citrus peels; (ii) fatty acid profiles, including both saturated and unsaturated fatty acids, with nutritional indices related to their health benefits; and (iii) the distribution of essential and non-essential elements—37 in total—among the three peels, including elements such as Ga, Ge, Nd, V, W, and Y, which rarely occur in foods, as well as those detected for the first time in clementine, mandarin, and orange peels in this study, including Al, As, Ba, Be, Bi, Cd, Co, Cs, Li, Mn, Mo, Ni, Pb, Rb, S, Sb, Sn, Sr, Ti, Tl, U, and Y. In addition, this work provides information on the daily intake of the analysed elements and their health risk values, parameters of significant importance before further use of citrus peel. By analysing the macro- and micronutrients using proximate chemical anal-

ysis, inductively coupled plasma mass spectrometry (ICP-MS), and gas chromatography (GC), this study provides an overview of the composition of three citrus peel varieties, highlighting their potential as functional value-added sources in reformulated foods and nutraceuticals. However, it should be noted that the presented data illustrate examples of the composition of these citrus peels, emphasising their valuable nutrient content. Further studies, including samples from diverse sources, are needed to determine a representative "typical" composition of clementine, mandarin, and orange peels.

2. Materials and Methods

2.1. Chemical and Reagents

All reagents, standards and solvents were of analytical quality. Glucose monohydrate and bovine serum albumin, which were used for the determination of sugars and proteins, were purchased from Sigma Aldrich (Darmstadt, Germany). Petroleum ether, sulphuric acid, copper sulphate, potassium iodide, potassium sodium tartarate and sodium hydroxide were purchased from Kefo (Zagreb, Croatia). Phenol was provided by Acros Organics (Geel, Belgium). Supelco 37-component fatty acid methyl ester mix, Supelco linoleic acid methyl ester mix and Supelco linolenic acid methyl ester isomer mix were purchased from Sigma-Aldrich (Darmstadt, Germany). Methanol (HPLC grade) was purchased from J.T. Baker (Philipsburg, PA, USA), potassium hydroxide (pro analysi) and sodium hydrogen sulphate monohydrate (pro analysi) from Kemika (Zagreb, Croatia) and isooctane (HPLC and GC grade) from Fisher (Pittsburg, CA, USA). Nitric acid (HNO_3, 65%, pro analysi) and hydrofluoric acid (HF, 48%, pro analysi) used for microwave-assisted digestion of peel samples were purchased from Kemika (Zagreb, Croatia). HNO_3 (68%, supra pur), which was used to acidify the samples prior to ICP-MS analysis, and In (50 µg/L), which served as an internal standard, were supplied by Fluka (Steinheim, Switzerland), and hydrofluoric acid (HF, 48%, supra pur) was supplied by J.T. Baker (Deventer, The Netherlands). The multi-element standard solution (100 ± 0.2 mg/L) containing Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V, W, Y and Zn, was purchased from Analytika (Prague, Czech Republic). The reference solution of K, Mg, Na, P and S (1000 mg/L) was also obtained from Analytika (Prague, Czech Republic). Citrus leaves (NCS ZC73018, China National Analysis Centre for Iron and Steel, Beijing, China) and apple leaves (NIST SRM 1515, The National Institute of Standards and Technology, Gaithersburg, MD, USA) were used as certified reference materials. The Milli-Q water used for the preparation of standards, samples and blanks was obtained using the Millipore purification system (resistance 18 MΩ-cm).

2.2. Plant Material

Orange (*Citrus sinensis*), mandarin (*Citrus reticulata*) and clementine (*Citrus clementine*) were purchased in local supermarkets (Zagreb, Croatia). The fruits were washed with tap water and distilled water, dried at room temperature and peeled with special care so as not to damage the active substances in the peel. The peels containing flavedo and albedo were cut into small pieces, crushed using a laboratory blender (Tefal, 180 W, GT 1108, China)(Grupe SEB, Mayenne, France), and immediately used for further analysis.

The particle size distribution of ground orange, mandarin, and clementine peels was analysed using a laser particle sizer (Mastersizer, 2000; Malvern Instruments, Worcestershire, UK). The measured particle sizes were as follows: orange peel: $d(0.1)$ = 250.483 µm, $d(0.5)$ = 710.625 µm, $d(0.9)$ = 1364.688 µm, $d(3.2)$ = 405.752 µm, $d(4.3)$ = 765.174 µm; mandarin peel: $d(0.1)$ = 151.812 µm, $d(0.5)$ = 600.906 µm, $d(0.9)$ = 1307.408 µm, $d(3.2)$ = 186.309 µm, $d(4.3)$ = 672.419 µm; clementine peel: $d(0.1)$ = 95.610 µm, $d(0.5)$ = 529.231 µm, $d(0.9)$ = 1278.651 µm, $d(3.2)$ = 99.348 µm, $d(4.3)$ = 614.598 µm. The most frequent particle size

ranges for the peels were: clementine 69.183–1659.587 µm, mandarin 104.713–1659.587 µm, and orange 120.226–1445.441 µm.

2.3. Chemical Analysis

Moisture content, total ash, total fat and total fibre content were determined according to the methods of the Association of Official Analytical Chemists [20]. Prior to the determination of total sugars and total proteins, the peel samples were extracted by heating under reflux at 50 °C for 1 h using water or phosphate buffer (pH = 7.4). The ratio of sample to solvent was 1:30 (*w*/*v*). The protein and sugar content was determined using the biuret method and the phenol-sulphuric acid method with a UV/Vis spectrophotometer (Perkin-Elmer Lambda 1, Mississauga, ON, Canada) at 540 and 490 nm, respectively. A brief description of all analyses can be found in the work by Ninčević Grassino et al. [21]. All experiments were performed in triplicate, and the results were expressed in g analytes per 100 g sample.

2.4. Fatty Acid Analysis by GC-FID in Clementine, Mandarin and Orange Peels

The total fat content was determined gravimetrically after the peel samples had been extracted for 8 h with petroleum ether in a Soxhlet apparatus [20]. Fatty acid methyl esters (FAMEs) were prepared by transesterification of each extract with methanolic potassium hydroxide solution according to the procedure described in EN ISO 12966-2 [22]. In brief, 60 mg of fat was weighed into a screw-capped plastic test tube and then 4 mL of isooctane was added. After dissolving the fat, 0.2 mL of methanolic potassium hydroxide solution (2 mol/L) was added using a micropipette. The contents of the tube were shaken vigorously for 1 min, allowed to stand for 2 min, then 0.5 g of sodium hydrogen sulphate monohydrate was added, and the contents of the tube were shaken. One mL of the upper isooctane layer containing FAME was taken for GC-FID analysis according to EN 12966-4 [23]. GC analysis was performed using a gas chromatograph, model Trace 1300 (Thermo Scientific, Waltham, MA, USA), equipped with a flame ionisation detector (FID) and an autosampler TriPlus RSH (Thermo Scientific, Waltham, MA, USA). The FAMEs were separated on a 60 m × 0.25 mm, 0.25 µm film thickness, DB-23 capillary column (Agilent Technologies, Palo Alto, CA, USA). The column temperature was initially maintained at 50 °C (1 min) and then increased at a rate of 25 °C/min to 175 °C or 4 °C/min to 230 °C. Helium was used as the carrier gas at a flow rate of 1.4 mL/min. The injector temperature was maintained at 250 °C and the injection volume was 1 µL at a split ratio of 1:100. GC Chromeleon 7.2 automatic chromatography software (Thermo Scientific, Waltham, MA, USA) was used for data acquisition and calculation by comparing the retention times of the standards. All analyses were performed in triplicate, and the results were expressed as g of fatty acid per 100 g of sample.

2.5. Fatty Acid Nutritional Indices in Clementine, Mandarin and Orange Peels

To assess the nutritional value of the fatty acids contained in orange, mandarin and clementine peels, the following indices were calculated according to the formulas of Chen et al. [24] and Montesano et al. [25], i.e., PUFA/SFA, PUFA/MUFA, MUFA/SFA, omega-3/omega 6, and omega-6/omega-3, where each of the abbreviations refers to the total amounts of polyunsaturated (PUFA), monounsaturated (MUFA), saturated (SFA), omega-3 and omega-6 fatty acids. In addition, the index of atherogenicity (IA), the index of thrombogenicity (IT) and the index of hypocholesterolaemia/hypercholesterolaemia (HH) were also calculated according to the formulae of Chen et al. [24].

2.6. Multi-Element Analysis by ICP-MS in Clementine, Mandarin and Orange Peels

For the multi-element analysis, the citrus peel subsamples (0.05 g), previously homogenised, were subjected to total digestion in a microwave oven (Multiwave 3000, Anton Paar, Graz, Austria) with a mixture of 6 mL HNO_3 (65% suprapur, Fluka, Steinheim, Switzerland) and 0.1 mL HF (48% pro analysi, J.T. Baker, The Netherlands) [26]. After completion of digestion, the samples were transferred into 100 mL volumetric flasks and brought to volume with Milli-Q water. Microwave digestion was carried out at 200 °C using a maximum power of 850 W, with a ramp time of 15 min, a hold time of 20 min, and a cooling period of 15 min.

Prior to analysis, the samples were prepared without further dilution, acidified with 2% v/v HNO_3 (68%, suprapur), and In (50 µg/L) was added as an internal standard. The blank sample was prepared in the same way as the peel samples. The total element concentration in the orange, mandarin, and clementine peels was determined using a triple quadrupole inductively coupled plasma mass spectrometer (Agilent 8900, ICP-QQQ)(Agilent Technologies, Inc., Santa Clara, CA, USA). The instrument conditions and data acquisition parameters used in this study were previously described by Petrović et al. [27] and are provided in the Supplementary Material (SM) in Table S1. Calibration curves were generated by external standardisation using a range of standard solutions, including a blank sample. For the quantification of selected elements, separate standard solutions were prepared as follows. The standard solutions for trace element determination were prepared by appropriate dilution of the multi-element standard solution (100 ± 0.2 mg/L). The calibration solution for all trace elements was prepared in a concentration range of 1–10 µg/L. A reference solution containing K, Mg, Na, P, and S (1000 g/L) was used to determine the main elements. The standard solutions for the quantification of the main elements were prepared in concentrations of 1 and 2 mg/L. The working standard solutions were prepared by adding 2% v/v HNO_3 (68%, suprapur, Fluka, Steinheim, Switzerland) and In (1 µg/L) as internal standard.

All samples were analysed for the total concentration of 37 elements (Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, K, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Rb, S, Sb, Se, Sn, Sr, Ti, Tl, U, V, W, Y and Zn). For quality control, the certified reference material citrus leaves (NCS ZC73018, China National Analysis Center for Iron and Steel, Beijing, China), was digested and analysed under the same conditions as the orange, mandarin, and clementine peels. Measured and certified element concentrations in the citrus leaves certified reference material are shown in Table S2 (Supplementary Material).

Limits of detection (LODs) were calculated as three times the standard deviation (3σ) of six consecutive measurements of element concentrations in the procedural blank [28].

The results of six replicates were expressed as the concentration of elements in mg per kg of sample.

2.7. Estimation of Element Intake from Clementine, Mandarin and Orange Peels

The estimated daily intake (EDI) of essential elements was based on the recommended daily allowance (RDA) or adequate intake (AI) from the Institute of Medicine [29] or the European Food Safety Authority (EFSA) [30]. The intake of non-essential, potentially toxic elements (Al, As, Cd, Pb and Sn) was estimated using the provisional tolerable weekly intake (PTWI) or the provisional tolerable monthly intake (PTMI) recommended by the Codex Alimentarius Commission [31]. As PTWI and PTMI were not established for other non-essential elements, their potential risk assessment was calculated using estimated daily intake (EDI), estimated weekly intake (EWI), and estimated monthly intake (EMI) based on a serving size of 100 g. In addition, the same serving size was used to calculate the target hazard quotient (THQ) according to Olaleye et al. [32], including the reference

dose (RfD) for each specific element (As, Ba, Cd, Li, Ni, Sb, Sr, and Y) from the Integrated Risk Information System (IRIS) database provided by the United States Environmental Protection Agency (USEPA) [33].

The EDI, EWI, and EMI, as well as PTWI and PTMI, were described by Koubová et al. [34]. However, the formulas provided in this work are based on a serving size of 100 g and a body weight of 60 kg for women and men aged 19 to 70 years. The EDI for essential elements (Ca, Co, Cr, Fe, K, Mg, Mn, Mo, Na, P, S, Se and Zn) was calculated using the following formulas: EDI = w (element in mg/kg) × serving size; EDI/RDA or EDI/AI in %. For non-essential elements (Al, As, Cd, Pb and Sn), the EDI was calculated in the same manner as for essential elements, while other estimated intakes are given by the following formulas: EWI = w (element in mg/kg) × serving size × days in one week; EMI* = w (element in mg/kg) × serving size × days in one month; PTWI = EWI/body weight; PTMI = EMI/body weight; PTWI/$PTWI_{JECFA}$ or PTMI/$PTMI^*_{JECFA}$ in %.

2.8. Statistical Analysis

The Shapiro–Wilk test was used to verify the normality of data from citrus peel samples. Accordingly, two tests were used to analyse correlations and variations in chemical characteristics between orange, clementine and mandarin peel samples: the parametric Anova test and the non-parametric Kruskal–Wallis test, depending on the distribution. The R package "heatmaply" and the standard "Euclidean" techniques for calculating the distance matrix were used to create the heatmap of the fatty acids in the peel. Multivariate principal component analysis (PCA) was performed to evaluate the distribution of elements based on their content among three peel types.

The biplot of the principal component analysis was visualised using the R packages "ggbiplot" and "ggplot2". The PCA scores associated with the first two components generated in the model were used to interpret the model. To determine whether there was a significant difference between the peels based on the PCA scores, a general linear model (GLM) was fitted using the aov function (analysis of variance) in R. All analyses were performed using R Core Team (v. 4.1.1) [35], with the significance level set at $p = 0.05$.

3. Results and Discussion

It is known that the chemical composition of citrus fruits is influenced by variety, cultivation method, time of harvest, degree of ripeness, storage period, and storage conditions [36]. In addition, numerous citrus fruit varieties differ in their chemical composition, as do the edible and non-edible parts such as pulp, peel, and seeds within the same variety. The results of this study present the chemical compositions of three citrus peel varieties—clementine, mandarin, and orange—including their macronutrient analysis, fatty acid profile, and multi-element composition, to provide an overview of their nutritional properties for sustainable use as value-added functional sources. Figure 1 outlines the analyses conducted, with the main findings described in the following paragraphs.

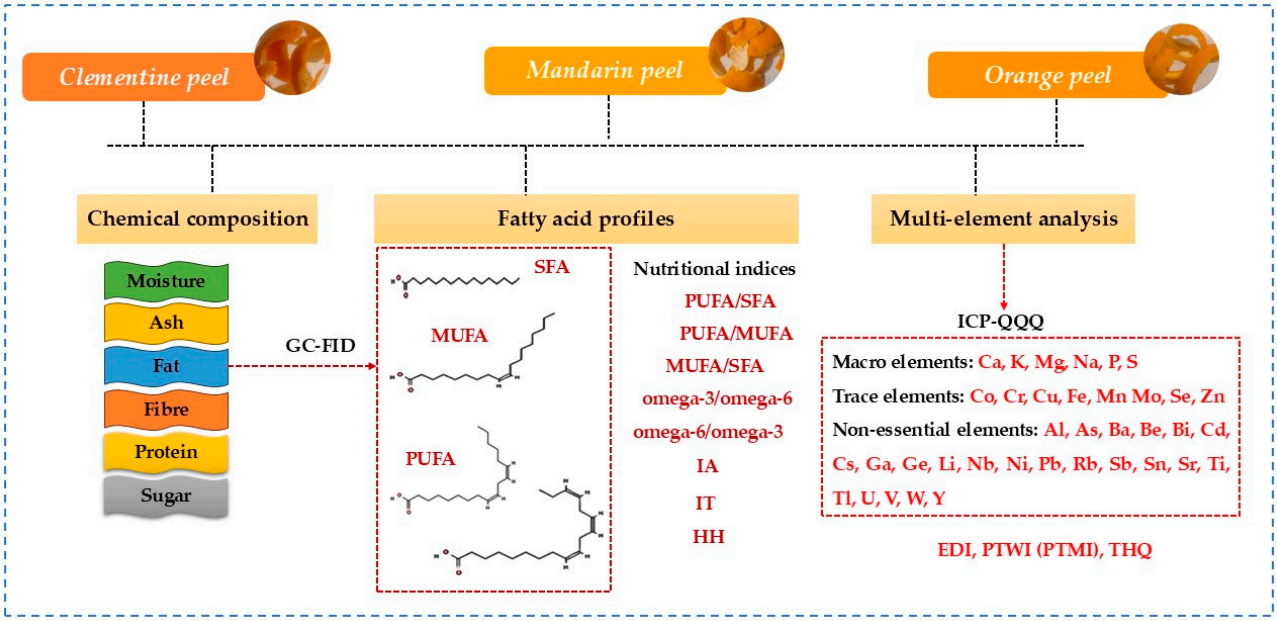


Figure 1. A schematic presentation of the analysis conducted on clementine, mandarin, and orange peels.

3.1. Chemical Composition of Clementine, Mandarin and Orange Peels

The results for the main chemical composition of clementine, mandarin, and orange peels are presented in Figure 2. These citrus peels have a moisture content of approximately 74%, specifically 74.7%, 74.5%, and 74.4%, respectively. Ash and fat contents are very low, at 1.00%, 1.14%, and 1.17%, and 0.95%, 1.01%, and 1.12% for clementines, mandarins, and oranges, respectively. Citrus peels are rich in fibre, with mandarins having the highest content at 65.0%, followed by oranges and clementines at 58.3% and 56.8%, respectively. As fibre is an important component of the human diet and contributes to gastrointestinal health [37], these citrus peels could support its intake. The total soluble protein content in orange, clementine, and mandarin peels is 2.1%, 2.8%, and 3.2%, respectively, while their total soluble sugar content is higher, at 31.8%, 37.0%, and 56.3%, respectively.

Shapiro–Wilk tests indicated that moisture, dry matter, ash and total fibre were normally distributed ($p > 0.05$), whereas fat, total protein and total sugars significantly deviated from normality ($p < 0.05$). As shown in Figure 2 and Table S3a,b in the Supplementary Material, there are no significant differences ($p \geq 0.05$) between clementine, mandarin, and orange peels in terms of moisture, ash, fat, and fibre content. However, the total soluble protein and sugar contents differ significantly ($p \leq 0.001$) between the peel types, which may be due to the complexity of the peel structure and the presence or absence of various compounds associated with proteins and sugars. Post hoc Dunn's test revealed a significant difference in total protein content between mandarin and orange ($p = 0.00029$), while clementine did not differ significantly from either mandarin or orange (Figure 2, $p = 0.154$ for both comparisons). For total sugars, a significant difference was observed between clementine and orange ($p = 0.00046$), whereas differences between clementine and mandarin ($p = 0.120$) and between mandarin and orange ($p = 0.251$) were not significant. In this context, the extent of their interactions influences the solubility of proteins and sugars in aqueous media (phosphate buffer and water), resulting in different yields for each peel.

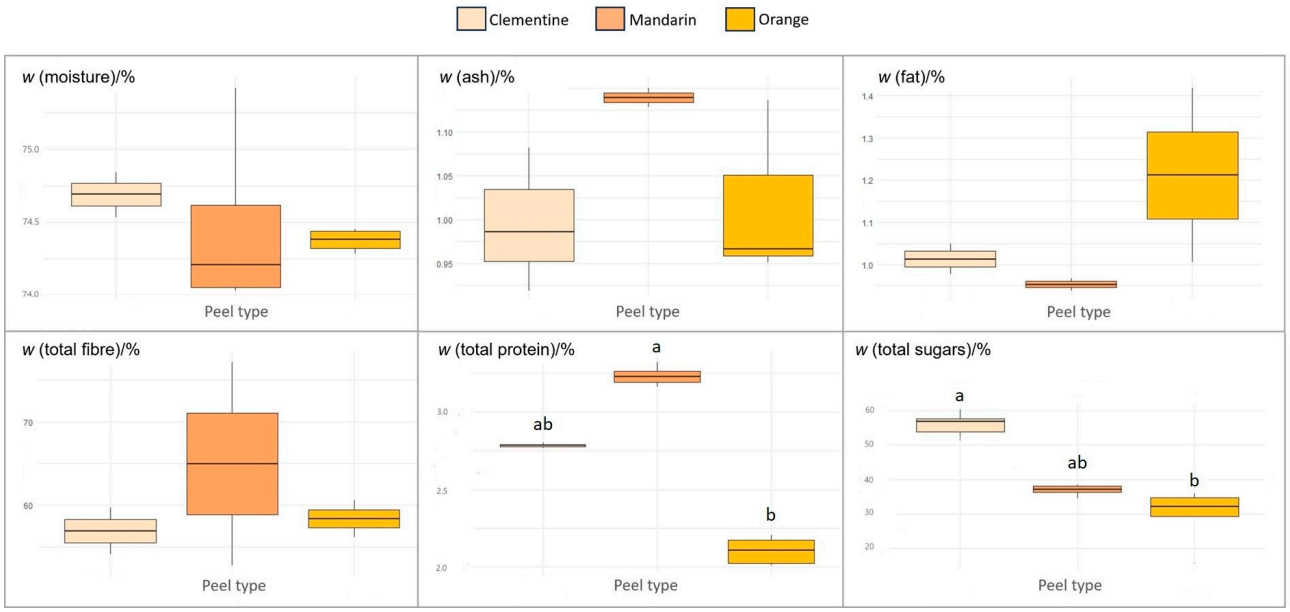


Figure 2. Boxplots of the main chemical composition of clementine, mandarin, and orange peels. Groups sharing the same letter do not differ significantly, whereas different letters indicate significant differences at $p < 0.05$. Where letters are not indicated, there was no statistically significant difference.

Although there are no reports in the literature on the main chemical compositions of the citrus peels analysed in this study, a comparison was made with some recently published papers to verify their quantities. The results for orange peel in this study agree with those of Özcan et al. [38], who reported a moisture content of 74.4%. Teixeira et al. [39] reported 89.2% for pear oranges (*Citrus sinensis*), and Matsuo et al. [40] reported 80.0% for all *Citrus natsudaidai* varieties. The moisture content in the peels of three extra early clementines (*Citrus clementina*) grown in Valencia is higher than the value found in this work, ranging from 82.5% to 88.1%, depending on the variety [41]. The moisture content is high both in these studies and in the fresh clementine, mandarin, and orange peels reported here, suggesting that the peel samples could be susceptible to chemical, physical, and microbiological alterations [42]. To avoid deterioration, the peels should therefore be used or further processed immediately after juice production, for example, by drying. In this context, Olfa et al. [43] applied three hours of drying at 105 °C and reported lower moisture values, namely 42.9% and 23.9% for mandarins and oranges, respectively. Özcan et al. [38] showed a significant decrease in moisture content after drying in the oven (11.4%), microwave (11.8%), and infrared (16.4%) compared to fresh orange peels (74.4%). Rafiq et al. [44] also reported lower moisture values of 3.0%, 4.9%, and 7.4% in vacuum, tray, and freeze drying compared to fresh kinnow (*Citrus reticulata*) peels (77.5%). Similar to this study, Teixeira et al. [39] found low ash values (0.89%) but higher fat values for fresh pear oranges (*Citrus sinensis*) than in this study. Rafiq et al. [44] also reported lower ash content (0.5%) and higher fat content (1.6%) for fresh kinnow (*Citrus reticulata*) peels. According to Matsuo et al. [40], the ash content of *Citrus natsudaidai* peels was 0.3% to 0.6%, depending on the variety. In comparison to this work, where high amounts of fibre and sugar were found, Teixeira et al. [39] reported 7.9% and 5.6% for pear orange peel (*Citrus sinensis*), and Rafiq et al. [44] showed values of 0.6% for fresh and 0.59%, 0.55%, and 0.63% for vacuum, tray, and freeze-dried kinnow peel (*Citrus reticulata*). According to Matsuo et al. [40], the total protein content of *Citrus natsudaidai* was between 0.4% and 1.1% for all varieties. Based on the data obtained, it can be concluded that clementine, mandarin, and orange peels can be classified as sources with low fat and protein content, and high moisture, fibre, and

sugar content. With this composition, they can be used to improve the quality of other foods, for example, in the production of jam [39] and cakes [45].

3.2. Fatty Acid Contents in Clementine, Mandarin and Orange Peels

In the fat extracts from clementine, mandarin, and orange peels, which were analysed using GC-FID, 19 fatty acids were detected, with polyunsaturated fatty acids (PUFAs) predominating. PUFAs play an essential role in maintaining general health, particularly through their influence on cardiovascular health, brain function, inflammation, and eye and skin health [46]. Among the PUFAs (Figure 3), linoleic acid (C18:2-9,12cis) and linolenic acid (C18:3-9,12,15cis) were present in the highest amounts. Clementine peels contain 30.1% linoleic acid, followed by orange (29.3%) and mandarin peels (23.9%). Clementine peels are also a major source of linolenic acid, with a content of 25.0%. Orange and mandarin peels contain lower proportions of linolenic acid, at 18.4% and 23.9% respectively. Among the other essential PUFAs, eicosatetraenoic acid (C20:4-8,11,14,17cis) is present at 1.3%, 3.1%, and 3.2% in orange, clementine, and mandarin peels, respectively. These citrus peels also contain eicosapentaenoic acid (20:5-5,8,11,14,17cis) at levels of 0.9% (mandarin), 1.3% (clementine), and 2.3% (orange). Although linoleic and linolenic acids predominate as omega-6 and omega-3 fatty acids in these citrus peel samples, the contribution of other PUFAs, which were found in lower amounts, is significant in terms of the total PUFA content and the total omega-6 and omega-3 fatty acid content (Figure 4). Their total amounts also include cervonic acid (C22:6-4,7,10,13,16,19cis), which was only found in orange peel at a level of 0.7%. The results show that clementine peels had the highest PUFA content at 59.6%, followed by very similar values for orange (52.0%) and mandarin peels (51.8%). Clementine peels also had the highest omega-3 fatty acid content at 29.5%, followed by slightly lower values for mandarin peels (27.9%) and orange peels (22.8%). The total content of omega-6 fatty acids is distributed as follows: clementine peels (30.1%) > orange peels (29.3%) > mandarin peels (23.8%), making clementine peels the dominant source of both omega-3 and omega-6 fatty acids.

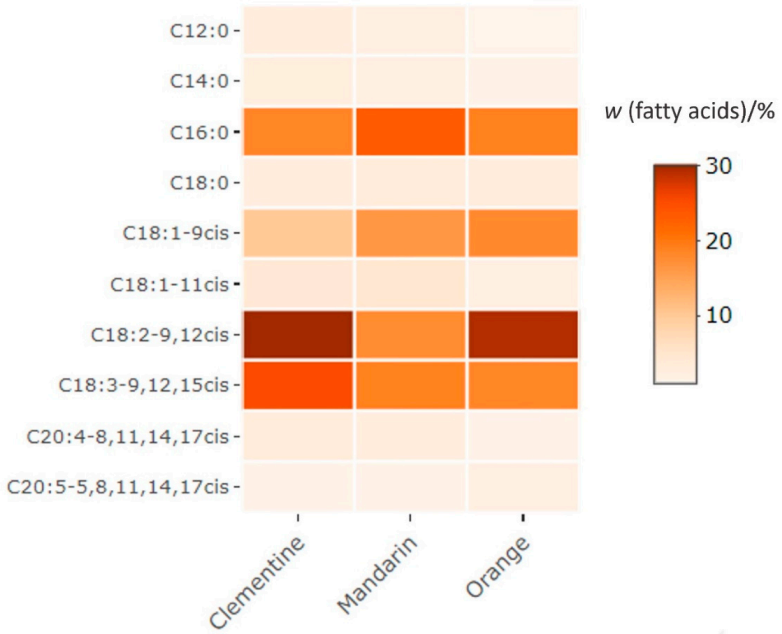


Figure 3. Heatmap of the individual fatty acids in clementine, mandarin, and orange peels after GC-FID analysis. C12:0—lauric acid, C14:0—myristic acid, C16:0—palmitic acid, C18:0—stearic acid, C18:1-9cis—oleic acid), C18:1-11cis—vaccenic acid, C18:2-9,12cis—linoleic acid, C18:3-9,12,15cis—linolenic acid, C20:4-8,11,14,17cis—eicosatetraenoic acid, 20:5-5,8,11,14,17cis—eicosapentaenoic acid.

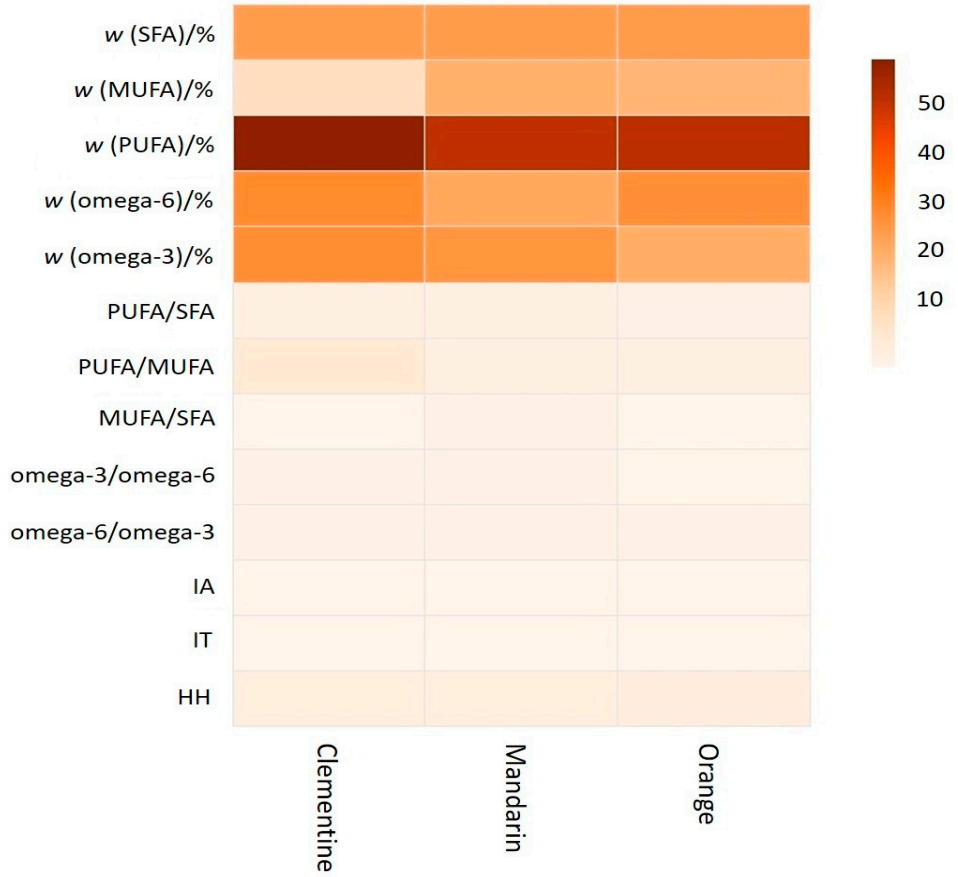


Figure 4. Heatmap of total fatty acids (SFA, MUFA, PUFA, omega-6, and omega-3) with nutritional indices (PUFA/SFA, PUFA/MUFA, MUFA/SFA, omega-3/omega-6, omega-6/omega-3, IA, IT, and HH) in clementine, mandarin, and orange peels after GC-FID analysis. SFA—saturated fatty acid, MUFA—monounsaturated fatty acid, PUFA—polyunsaturated fatty acid, IA—index of atherogenicity, IT—index of thrombogenicity, HH—index of hypocholesterolaemia/hypercholesterolaemia.

While both types of PUFAs are necessary for health, an imbalance with excessive omega-6 intake relative to omega-3 may contribute to inflammation and increase the risk of chronic disease [47,48]. The overall distribution of omega-6 and omega-3 fatty acids in the peels is closely related to the omega-6/omega-3 and omega-3/omega-6 ratios, with values of 0.9, 1.0 and 1.3, and 1.2, 1.0 and 0.8 for mandarin, clementine and orange peels, respectively, confirming their different proportions among the peels. In addition to PUFAs, clementine, orange and mandarin peels also contain monounsaturated fatty acids (MUFAs), with oleic acid (C18:1-9cis) predominating at 8.0%, 16.1% and 17.7% in clementines, mandarins and oranges, respectively (Figure 3). Oleic acid has been associated with various health benefits, such as heart health, anti-inflammatory effects, blood sugar control, brain function and skin health [49], so these by-products can be considered a valuable source of oleic acid. In addition to oleic acid, vaccenic acid (C18:1-11cis) is also present in orange, clementine and mandarin peels at lower levels of 2.2%, 2.3% and 4.5%, respectively. These amounts contribute significantly to the total MUFA content of 10.2% (clementine), 20.7% (orange) and 21.9% (mandarin), with significantly higher values found in mandarin peel (Figure 4). The results of this study show that the citrus peels evaluated have a high content of unsaturated (poly- and mono-) fatty acids, up to 69.8%, 71.7% and 73.6% for clementine, orange and mandarin, respectively. Their PUFA/MUFA ratios are as follows: 2.37 (mandarin), 2.51 (orange) and 5.82 (clementine), making them a good source for dietary intake. Not only this study, but also that of Matsuo et al. [40] reports that the fatty acids in three *Citrus natsudaidai* peel varieties are unsaturated and account for about 70% of

the total fatty acid content. Mohamed Ahmed et al. [50] also showed that unsaturated fatty acids are widely distributed in citrus peels of bitter oranges, mandarins and grapefruits. They reported oleic acid contents of 20.3%, 27.6% and 40.3% and linoleic acid contents of 30.5%, 35.6% and 29.3% for bitter oranges, mandarins and grapefruits, respectively. Jahromi et al. [51] determined oleic acid contents of 9.8%, 17.1%, 19.9% and 20.8% and linoleic acid contents of 30.1%, 30.3%, 33.2% and 33.9% for mandarins, grapefruits, bitter and sweet oranges. In comparison to this study, Mohamed Ahmed et al. [50] determined lower amounts of linolenic acid: 17.3% (bitter orange), 9.2% (mandarin) and 3.4% (grapefruit), indicating differences between the varieties. Jahromi et al. [51] reported linolenic acid contents of 6.4% (mandarin), 8.2% (bitter orange), 15.4% (mandarin) and 16.1% (grapefruit). Although the values for oleic and linoleic acid obtained in this study are almost the same as those reported in other works, the amounts of linolenic acid are slightly higher, which depends on the citrus peel varieties. Thus, our results show the importance of reusing clementine, mandarin and orange peels due to their valuable unsaturated fat profile.

For comparison, the fruits of bitter orange, lemon, mandarin and orange, as shown by Lamine et al. [52], contain linoleic acid in amounts of 21.8%, 29.2%, 32.8% and 32.2%, respectively, which are similar to those of the peels analysed in this study. Oleic acid in bitter oranges, oranges and mandarins is present in amounts of 15.4%, 10.6% and 4.3%, respectively, whereas it is not found in lemons. Linolenic acid is found only in mandarins (19.8%) and lemons (25.8%), with amounts similar to those in this study, further emphasising the importance of using these peels. In addition to PUFAs and MUFAs, the peels of clementines, mandarins and oranges also contain saturated fatty acids (SFAs), among which palmitic acid (C16:0) predominates, with contents of 17.6% (mandarin), 18.3% (clementine) and 18.9% (orange) (Figure 3). Stearic acid (C18:0), the second most abundant SFA, contributes 2.3% (clementine), 2.9% (orange) and 3.2% (mandarin), followed by myristic acid (C14:0) at 1.3% (orange), 2.1% (mandarin) and 2.3% (clementine). These acids mainly contribute to the total SFA contents, with values of 25.9%, 26.0% and 26.8% for mandarin, clementine and orange peels, respectively, which affect the overall PUFA/SFA and MUFA/SFA ratios. The following PUFA/SFA ratios can be given regardless of peel type: 1.94 (orange), 2.00 (mandarin) and 2.30 (clementine), and for the MUFA/SFA ratio: 0.39 (clementine), 0.77 (orange) and 0.84 (mandarin). These results indicate that all the peels analysed can make a significant contribution to cardiovascular health, considering that higher PUFA/SFA and MUFA/SFA ratios have a more positive effect on health quality. For comparison with other materials analysed, such as algae, plants, vegetable oil, shellfish, fish, meat and dairy products, the PUFA/SFA indices range between 0.02 and 6.96 [24]. In addition to the PUFA/SFA, MUFA/SFA, omega-6/omega-3 and omega-3/omega-6 ratios, other health-related indices, such as IA, IT and HH (Figure 4), also showed differences between the nutritional and health-related properties of clementine, mandarin and orange. For example, the lowest IA was found for oranges (0.34), followed by mandarins (0.41) and clementines (0.47). As a lower IA value indicates better lipid quality for cardiovascular health, reflecting a higher proportion of beneficial unsaturated fats compared to harmful saturated fats [24], orange peels appear to be a slightly better source of value added than mandarins and clementines. Similar IA values of 0.44 and 0.48 were reported by Lamine et al. [52] for orange and mandarin pulp, respectively. Like the IA value, lower IT values also indicate a reduction in potential heart attacks or strokes, and the results showed no significant differences between the oil peels assessed. The values of 0.20 (orange), 0.23 (clementine) and 0.24 (mandarin) obtained in this work are lower than those reported by Jahromi et al. [51] and Lamine et al. [52], who showed IT values of 0.53 and 0.75 for mandarin and orange peels, and 0.34 and 1.21 for mandarin and orange pulp. The HH index focuses on the balance between cholesterol-lowering and cholesterol-increasing fatty

acids and is therefore particularly useful for classifying foods and oils based on their potential effects on cholesterol metabolism, as is the case in this work. Lower HH values indicate that the lipid source may contribute to elevated cholesterol levels and associated risks, while higher HH values indicate a more favourable ratio of hypocholesterolaemic to hypercholesterolaemic fatty acids, making the lipid source healthier for cardiovascular diseases. The results for the HH value are lowest for clementines (2.91), followed by mandarins (3.13) and oranges (3.26). In comparison, oranges and mandarins had HH values of 1.82 and 2.56, respectively [52], making the peels analysed in this work a promising, valuable, functional source.

While our findings highlight variations in fatty acid profiles across different citrus cultivars, these profiles and contents could be further evaluated considering other factors, including the growing conditions of citrus fruit and peel, such as climate, soil properties, fruit maturity, storage conditions, and the structural role of lipids in the peel cuticle. These factors are crucial for a more comprehensive nutritional overview of the quality and quantity of fatty acids in citrus peel.

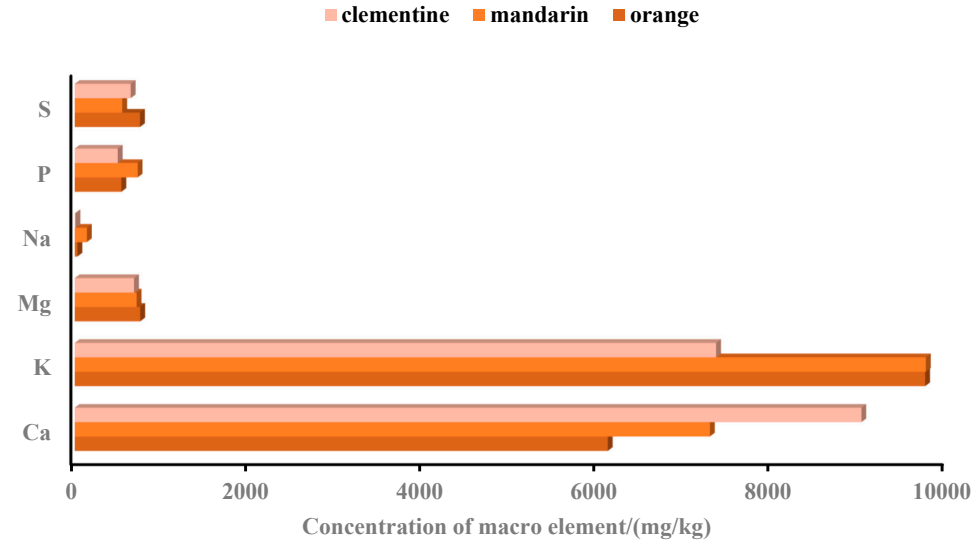
3.3. Multi-Element Content in Clementine, Mandarin and Orange Peels

In this study, a multi-element analysis of clementine, mandarin, and orange peels was conducted to assess their potential for reuse as a functional source of various value-added elements. The results of the analysed elements, presented in Table S4, Supplementary Material, were categorised as essential and non-essential and are discussed in the following sections.

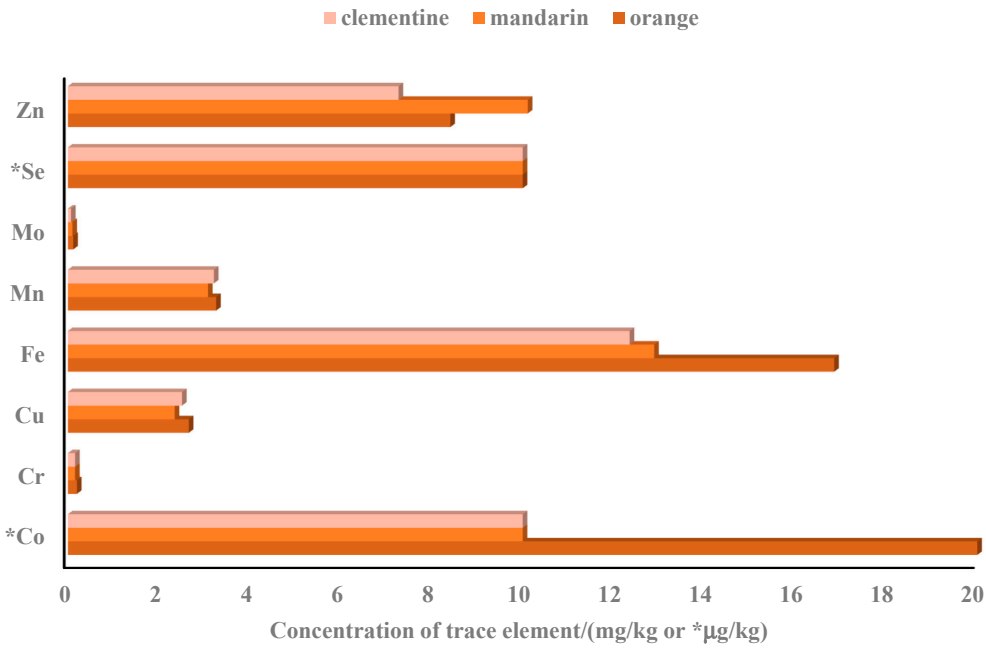
3.3.1. Essential Macro Elements

Calcium, potassium, magnesium, sodium, phosphorus and sulphur are the most important essential macro elements in the peels of clementines, mandarins and oranges. Their distribution is uneven (Figure 5a), with the highest potassium content found in mandarin (9766 mg/kg) and orange peels (9758 mg/kg), followed by clementine peels (7357 mg/kg). Orange and mandarin peels also contain higher magnesium levels (752 and 710 mg/kg, respectively) than clementine peels (681 mg/kg). Orange peels are a good source of sulphur, with a content of 758 mg/kg, followed by clementine (642 mg/kg) and mandarin peels (545 mg/kg). Conversely, mandarin peels have higher phosphorus (722 mg/kg) and sodium (139 mg/kg) contents than orange and clementine peels (535 and 493 mg/kg for phosphorus, and 31 and 9.25 mg/kg for sodium, respectively). Although clementine peels contain lower amounts of essential macro elements compared to mandarin and orange peels, this by-product is a valuable source of calcium (9026 mg/kg), followed by mandarin (7285 mg/kg) and orange peels (6114 mg/kg). As calcium plays an important role in building hard, strong bones [53], the contribution of peels to the daily calcium requirement should not be overlooked. For example, clementine peels can provide 75.2% of the daily calcium requirement, while mandarin and orange peels provide 60.7% and 51.0%, respectively (Table 1). The contribution of the three peel types to the daily potassium requirement is lower than that of calcium and is similar for clementines (21.0%), oranges (27.9%) and mandarins (27.9%). The daily requirements for other elements, such as magnesium, phosphorus and sodium, are lower than those for calcium and potassium, so clementine, mandarin and orange peels cover 16.2%, 16.9% and 17.9% of the daily magnesium requirement, respectively. Along with calcium, phosphorus is also involved in the formation of strong bones and teeth, and its daily requirement is met at 7.0%, 7.7% and 10.3% by clementine, orange and mandarin peels, respectively. The contribution of mandarin, orange, and clementine peels to the daily sodium requirement is lowest, with values of 0.9%, 0.2%, and 0.1%, respectively. The RDA value for sulphur was not determined, as

deficiency is not considered frequent. It is assumed that an intake of about 850 mg/day is sufficient to meet the body's basic requirements [54]. According to the results, mandarins, clementines and oranges provide 54.5, 64.2 and 74.9 mg/day of sulphur, respectively, based on a 100 g portion size.

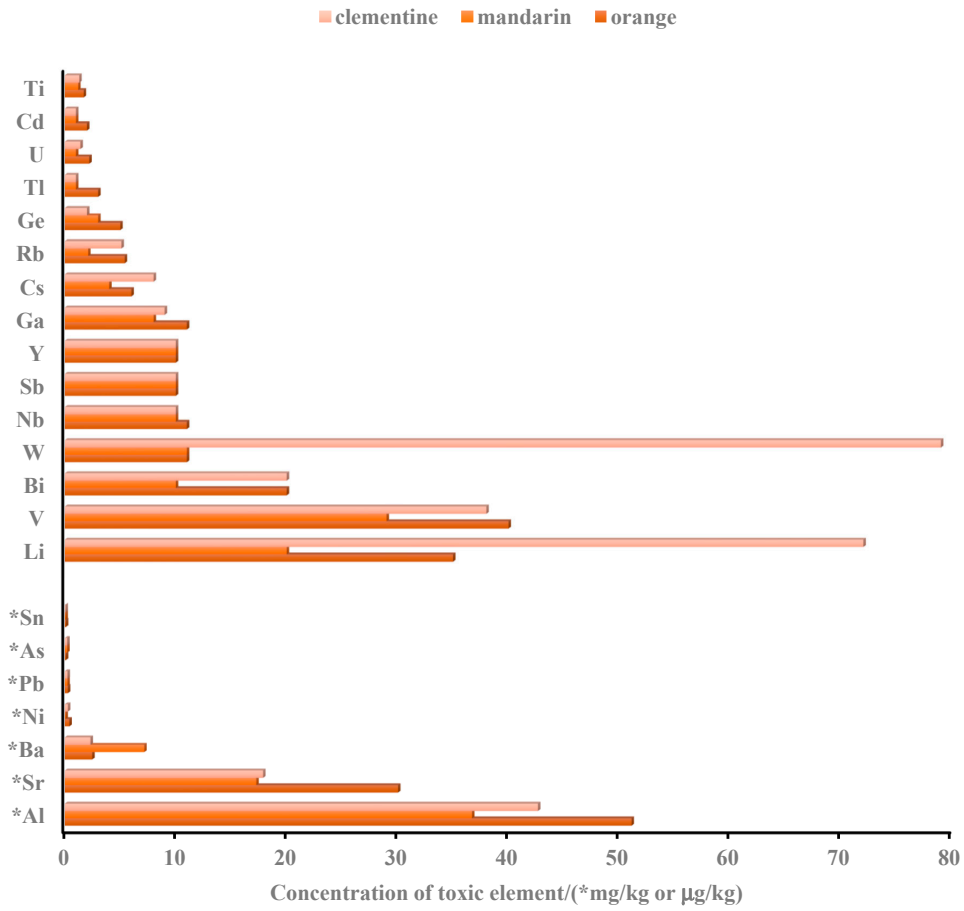


(**a**)



(**b**)

Figure 5. *Cont.*



(**c**)

Figure 5. (**a**) Concentration of essential macro elements in clementine, mandarin, and orange peels according to ICP-QQQ analysis. (**b**) Concentration of essential trace elements in clementine, mandarin and orange peels according to ICP-QQQ analysis. (**c**). Concentration of non-essential elements in clementine, mandarin and orange peels according to ICP-QQQ analysis. Asterisk in (**b**) means: Instead of μg/kg, the values for Al, Sr, Ba, Ni, Pb, As and Sn were expressed in mg/kg. Asterisk in (**c**) means: Instead of mg/kg, the values for Cr and Se were expressed in mg/kg.

Similar to this study, Czech et al. [55] also showed that K and Ca predominate in orange and mandarin peels, followed by P, Mg, and Na. However, the values determined in their study are lower than those found in this work. Hayat et al. [56] reported a K content of 9330 to 9460 mg/kg in kinnow peel, similar to the present study. The Ca content ranges from 6115 to 6475 mg/kg, which corresponds to the Ca content in orange peels, while the P values are between 640 and 680 mg/kg, matching the P content in three types of peels. Hayat et al. [54] also showed that the Mg content is between 550 and 560 mg/kg, which is slightly lower than the value found in this work, regardless of peel type. In contrast, the Na contents are higher than those found in this work, ranging from 515 to 590 mg/kg. For further comparison, the pomelo peels analysed by Sharma et al. [57] follow the same macro element distribution trends as in this work, although the values are lower, i.e., K (1270 mg/kg) > Ca (288 mg/kg) > Mg (230 mg/kg) > P (219 mg/kg) and Na (6.8 mg/kg). The low values of Ca (5158 mg/kg), K (87.5 mg/kg), and Mg (53.9 mg/kg) for pomelo peels are also reported by Ani et al. [58] and in this study. However, they reported higher levels of P (3666 mg/kg) and Na (2748 mg/kg) compared to this study. Therefore, we hypothesise that the differences in macro element content between this study and other literature reports are likely influenced by citrus variety, geographical origin, and environmental and soil conditions during cultivation.

Table 1. Estimated daily intake (EDI) of essential elements from clementine, mandarin and orange peels according to ICP-QQQ analysis.

Element	RDA (mg/day)	AI (mg/day)	UL (mg/day)	Clementine Peel		Mandarin Peel		Orange Peel	
				EDI (mg/day)	(%)	EDI (mg/day)	(%)	EDI (mg/day)	(%)
Ca	1000–1200			903	(75.2)	729	(60.7)	611	(51.0)
K	3100–3500	4700	n.a.	736	(21.0)	977	(27.9)	976	(27.9)
Mg	310–420	n.a.	350	68	(16.2)	71	(16.9)	75	(17.9)
Na	n.a.	1200–1500	2300	0.9	(0.1)	14	(0.9)	3	(0.2)
P	700			49	(7.0)	72	(10.3)	54	(7.7)
S	n.e.	n.e.	n.e.	64.3	/	54.5	/	74.9	/
Cu	0.9	n.a.	10	0.3	(27.9)	0.2	(26.1)	0.3	(29.6)
Fe	8–18	n.a.	45	1.2	(6.9)	1.3	(7.2)	1.7	(9.4)
Mn	n.a.	1.8–2.3	11	0.3	(14.0)	0.3	(13.4)	0.3	(14.3)
Zn	8–11	n.a.	40	0.7	(6.6)	1.0	(9.2)	0.8	(7.7)
Co	n.a	n.a	n.a	0.001	/	0.001	/	0.002	/
Cr	n.a.	0.020–0.035	n.a.	0.016	(45.7)	0.016	(45.7)	0.02	(57.1)
Mo	0.034–0.045	n.a.	2	0.01	(15.6)	0.01	(28.6)	0.012	(26.7)
Se	0.055	n.a	0.4	0.001	(1.8)	0.001	(1.8)	0.001	(1.8)

RDA—recommended daily allowance, AI—adequate intake, UL—tolerable upper intake level, EDI/RDA or EDI/AI in %; n.a. not available; n.e. not estimate.

3.3.2. Essential Trace Elements

The content of essential trace elements in clementine, mandarin and orange peel decreases in the following order: Fe > Zn > Mn > Cu > Cr > Mo > Co > Sn (Figure 5b). The highest Fe content is found in orange peel (16.9 mg/kg), followed by mandarin (12.9 mg/kg) and clementine (12.4 mg/kg). These values are higher than those reported by Czech et al. [55], who found 3.3 and 5.1 mg/kg Fe in mandarin and orange peel, respectively. In comparison, Hayat et al. [56] reported even higher Fe values for microwaved and non-microwaved kinnow peel, at 110 and 131 mg/kg, respectively. Considering the RDA values for Fe (Table 1) and the importance of its intake for individuals with iron deficiency, the results of this study show that clementine, mandarin and orange peel each provide about 7 to 9% of the daily Fe requirement. The second most abundant essential trace element is Zn, with mandarin peel containing 10.1 mg/kg, followed by orange (8.4 mg/kg) and clementine (7.3 mg/kg). The RDA for Zn is between 8 and 11 mg/day (Table 1), so Zn from these peels can also cover up to 7 to 9% of the daily requirement. The three peels analysed are a good source of Mn, with values of 3.1, 3.2 and 3.3 mg/kg for mandarin, clementine and orange, respectively, covering 13 to 14% of the daily Mn requirement. In addition to Mn, these peels can also meet the daily requirement for Cu, with values between 26 and 30%, depending on the type of peel. Mandarin contains 2.4 mg/kg Cu, clementine 2.5 mg/kg and orange 2.7 mg/kg. Other essential trace elements, such as Cr, Mo, Co and Se, are present in very small quantities. Among these, Se has the lowest value (0.01 mg/kg, Table S4, Supplementary Material), so all three types of peel can supply 1.8% of the daily Se requirement based on the RDA. The Cr, Mo and Co contents are slightly higher, ranging from 0.16 to 0.20 mg/kg, 0.07 to 0.12 mg/kg and 0.01 to 0.02 mg/kg, respectively, depending on the type of peel (Table S4, Supplementary Material). Taking into account their RDA or AI values (Table 1), with the exception of Co (RDA not available), the proportion of Mo and Cr in the daily requirement provided by the peels is 16 to 29% and 46 to 57%, respectively. Although cobalt and chromium are essential for humans in ultra-trace concentrations, excessive intake can make them potentially toxic. Considering that the quantities of chromium and cobalt obtained in this study are lower than those proposed by the Institute of Medicine [29], regardless of the adequate intake (0.020–0.035 mg/day), and those of EFSA [59] (0.057 to 0.084 mg/day) for daily chromium intake, as well as EFSA's suggestion that values of 14 µg/day for cobalt should not be exceeded [60], the peels of clementine, mandarin, and orange should be considered safe for consumption.

3.3.3. Non-Essential Elements

Non-essential elements, unlike essential ones, do not provide beneficial effects for humans, and their presence in food and, consequently, in the diet can be harmful or toxic. Among the non-essential elements identified in this study—such as Al, As, Ba, Bi, Cd, Cs, Ga, Ge, Li, Nb, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V, W, and Y—aluminium predominates, with concentrations ranging from 36.7 to 51.1 mg/kg, depending on the type of peel (Figure 5c). As the estimated PTWI of Al for the three peels ranges from 428 to 596 µg/kg body weight (Table 2), consumption of clementine, mandarin, and orange peels does not appear to have any toxic effects on health. The PTWI values for the evaluated citrus peels are below the reference value of 1000 µg/kg body weight established by the Codex Alimentarius Commission [31]. In addition to this reference value, EFSA [61] has also reported a dietary exposure range for Al of 1.6 to 13 mg per day, corresponding to 0.2 to 1.5 mg/kg body weight per week for a 60 kg adult. Comparing the Al exposure data provided by EFSA [61] with that found in this study further confirms the non-toxic effect of Al from the analysed peels. According to the data (Table 2), the EDI of Al from mandarin, clementine, and orange is 3.67, 4.27, and 5.11 mg/day, respectively, corresponding to 0.43, 0.50, and 0.60 mg/kg

body weight per week, which falls within the range established by EFSA [61]. Considering that the tolerable weekly intake of aluminium recommended by EFSA [61] is 1 mg/kg of body weight per week, and that the values in this work were below this established limit, consumption of the peels, regardless of aluminium content, will be safe.

In addition to Al, PTWI or PTMI values were also provided for Pb, As, Cd, and Sn [31] as metals with particularly toxic effects. The reference PTWI for As (15 μg/kg body weight), although withdrawn [31], is higher than the values found for clementine (2.5 μg/kg/bw), mandarin (2.5 μg/kg/bw), and orange (1.1 μg/kg/bw), confirming the non-toxic effect of As. For Pb, the PTWI value of 25 μg/kg body weight was also withdrawn as it did not provide adequate health protection. However, as with As, this dose continues to be used in the absence of other suitable guidance, in addition to that of USEPA [33]. The estimated PTWI values of Pb for the three citrus peels are also below the reference value (Table 2), indicating no adverse effects on human health. For Cd, the reference values expressed as monthly intake (PTMI) of 25 μg/kg body weight are also higher than the estimated PTMI values of 0.05 μg/kg/bw for clementine and mandarin, and 0.10 μg/kg/bw for orange, indicating that their consumption would not have a toxic effect. Besides PTWI or PTMI values provided by the Codex Alimentarius Commission [31], the maximum permitted levels of Cd, As, Pb, and Sn have been set for various foodstuffs by EU Commission Regulation No. 1881/2006 [62]. Considering that their contents of 0.001–0.002 mg/kg (Cd), 0.06–0.09 mg/kg (Sn), 0.09–0.21 mg/kg (As), and 0.23–0.27 mg/kg (Pb) found in this study are below the established maximum permitted levels of 0.05–1 mg/kg (Cd), 0.1–0.25 mg/kg (As), 0.02–1.5 mg/kg (Pb), and 50–200 mg/kg (Sn), consumption of the three citrus peels would not have any toxic effect. In contrast to the PTWI and maximum permitted values of As, according to the Codex Alimentarius Commission [31] and EU Commission Regulation No. 1881/2006 [62], the THQ data indicated potential As toxicity. As the THQ values are 5.59 for clementine and mandarin peels, and 2.39 for orange (Table 3), a THQ > 1 signifies a probability of non-carcinogenic health risk. Due to variations in the recommendations used and the potential toxicity of this element, its monitoring must be ensured. This proposal aligns with Food and Drug Administration (FDA) [63] criteria, which require that dietary exposures to arsenic and other heavy metals be measured over time. In addition to controlling arsenic levels in food products due to its hazardous effects on humans [64], it is necessary to reduce the use of agrochemicals, including pesticides and fertilisers, which commonly contain arsenic, especially during the initial stages of plant cultivation. The crop growing environment, arsenic absorption from soil and water by crops, and subsequent crop ingestion by humans—whether in raw form, as in the case of citrus peel evaluated in this study, or through crop processing—are the main reasons for arsenic toxicity.

Table 2. Provisional tolerable weekly (PTWI) and monthly (PTMI*) intake of toxic elements (As, Al, Cd, Pb and Sn) from clementine, mandarin and orange peels according to ICP-QQQ analysis.

Peel	JECFA PTWI or PTMI* (µg/kg bw)	EDI (µg)	EWI or EMI* (µg)	PTWI or PTMI* (µg/kg bw)	PTWI/PTWI$_{JECFA}$ (%) or PTMI/PTMI*$_{JECFA}$ (%)
			Cd		
Clementine	25 *	0.1	3 *	0.1 *	(0.2 *)
Mandarin		0.1	3 *	0.1 *	(0.2 *)
Orange		0.2	6 *	0.1 *	(0.4 *)
			Sn		
Clementine	14,000	6	42	0.7	(0.01)
Mandarin		9	42	0.7	(0.01)
Orange		9	63	1.1	(0.01)
			Pb [a]		
Clementine	25	24	168	2.8	(11.2)
Mandarin		23	161	2.7	(10.7)
Orange		27	189	3.2	(12.6)
			Al		
Clementine	1000	4265	29,855	498	(49.8)
Mandarin		3671	25,697	428	(42.8)
Orange		5109	35,763	596	(59.6)
			As [a]		
Clementine	15	21	147	2.5	(16.3)
Mandarin		21	147	2.5	(16.3)
Orange		9	63	1.1	(7.0)

JECFA—Joint Food and Agriculture Organization/World Health Organization (FAO/WHO) Committee on Food Additives, EDI—estimated daily intake, EWI—estimated weekly intake, EMI*—estimated monthly intake, PTWI/PTWI$_{JECFA}$ or PTMI/PTMI*$_{JECFA}$. [a] PTWI values of 25 and 15 µg/kg bw for Pd and As, respectively are withdrawn by JECFA. * means Only the values for Cd are expressed as monthly intake.

Table 3. Estimated daily intake (EDI) and target hazard quotient (THQ) of toxic elements (Sr, Ba, Ni, As, Li, Sb, Y and Cd) from clementine, mandarin and citrus peels according to ICP-QQQ analysis.

Element	IRIS	Clementine Peel		Mandarin Peel		Orange Peel	
	RfD (mg/kg/day)	EDI (mg/kg/day)	THQ	EDI (mg/kg/day)	THQ	EDI (mg/kg/day)	THQ
Sr	0.6	0.029	0.048	0.028	0.046	0.048	0.080
Ba	0.2	0.004	0.019	0.114	0.057	0.004	0.020
Ni	0.02	0.0004	0.022	0.0001	0.005	0.001	0.033
As	0.00006	0.0003	5.594	0.0003	5.594	0.0001	2.397
Li	0.003	0.0001	0.038	0.00003	0.011	0.00006	0.019
Sb	0.0004	0.00002	0.040	0.00002	0.040	0.00002	0.040
Y	0.009	0.000001	0.001	0.000001	0.001	0.000001	0.001
Cd	0.001	0.000002	0.002	0.00002	0.002	0.000003	0.002

IRIS—Integrated Risk Information System, RfD—reference dose.

Besides Al, which was found in the highest amounts, the evaluated citrus peels also contained high levels of Sr, ranging from 17.2 to 30.0 mg/kg, depending on the type of peel (Figure 5c). Other elements, such as Ba and Ni, were found in ranges of 2.3 to 7.2 mg/kg and 0.1 to 0.4 mg/kg, respectively, and their THQ values below 1 (Table 3) indicate safe non-carcinogenic levels. Additionally, Y and Sb, detected in quantities of 8 and 10 μg/kg, respectively, did not show any health risk (THQ < 1 for all analysed peels). Other rare elements for which PTWI, PTMI, and RfD have not been established include V and W, found in amounts of 11–79 μg/kg and 29–40 μg/kg, respectively. Both elements, due to environmental diffusion and accumulation in soil, could be transmitted to humans by inhalation, ingestion, and absorption [65,66]. Exposure through these pathways could cause respiratory damage and lung cancer, immunological and gastrointestinal disturbances, as well as hepatic, renal, and bone toxicity [67–69]. In comparison to V and W, lower quantities were found for Bi (10–20 μg/kg), Nb (10–11 μg/kg), and Ga (8–11 μg/kg) in citrus peel. Cs, Rb, Ge, Tl, U, and Ti were detected in the lowest amounts, ranging from 1 to 8 μg/kg. As there are no established recommendations for dietary intake of these elements, nor detailed data on their levels in other literature reports for clementine, mandarin, and orange peels, it was difficult to discuss and compare the data obtained in this study. As with As, we therefore recommend their continuous monitoring, especially if peels are to be used as functional ingredients in newly formulated foods.

3.4. Principal Component Analysis of Essential and Non-Essential Elements in Clementine, Mandarin and Orange Peels

Due to the common application of principal component analysis (PCA) in food sample analysis [70,71], PCA was also implemented in this study to identify the distribution of essential and non-essential elements among clementine, mandarin, and orange peels. The first two principal components (PCs) explained 70.0% of the total variance, with PC1 accounting for 45.7% and PC2 for 24.0% (Figure 6). The biplot generated using PC1 and PC2 illustrates the alignment of variables (elements) and samples (clementine, mandarin, and orange peels) with respect to the principal components. Measurements were grouped by 99% confidence interval ellipses around the centroids of each peel. According to PC1, mandarin and clementine peels were in the positive area, separated from orange peels, which were in the negative area. According to PC2, orange and mandarin peels were separated from clementine peels, which were in the negative area. Clementine peels were characterised by Li, W, Ca, and As; mandarin peels by Ba, P, and Na; and orange peels by other elements, including essential (Co, Cr, Cu, Fe, K, Mn, Mg, Mo, S, Se, and Zn) and non-essential (Bi, Cd, Cs, Ga, Ge, Ni, Nb, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, and Y) elements.

The results showed that the distribution of elements is significantly different ($p < 0.001$) among the three citrus peels. Their contribution to the model is presented in Table S5 (Supplementary Material) by principal component loadings, where loadings with large absolute values correspond to variables with greater discriminating ability. The highest loadings in PC1 were: Al (−0.238) > Co (−0.236) > Fe (−0.232) > Bi (−0.228), while in PC2: Li (−0.321) > Na and P (0.307) > W (−0.302) > K (0.298) > Se (−0.282) > Ba (0.280) > Rb (−0.262), confirming their significant contribution to the model. The negative coefficients (Table S5, Supplementary Material) and consequently negative correlations (Figure 6) based on PC1 showed all elements included in the orange peel area. Cd, Co, Cs, Cu, Mn, Ni, Rb, Se, S, and U are also negatively correlated based on PC2, whereas Bi, Cr, Ga, Ge, Fe, K, Mg, Mo, Nb, Pb, Sn, Sr, Ti, Tl, Zn, and Y are positively correlated. The dominant elements in the clementine area (Li, W, Ca, and As) based on PC1 loadings had a positive correlation, and a negative correlation with PC2. For mandarin, Na, P, and Ba as dominant elements had positive loadings with both PC1 and PC2. Thus, using the input data of essential and non-essential elements, it is shown that the determined elements have a non-unique distribution among peels, classifying peels in this manner as their valuable (or not) sources.

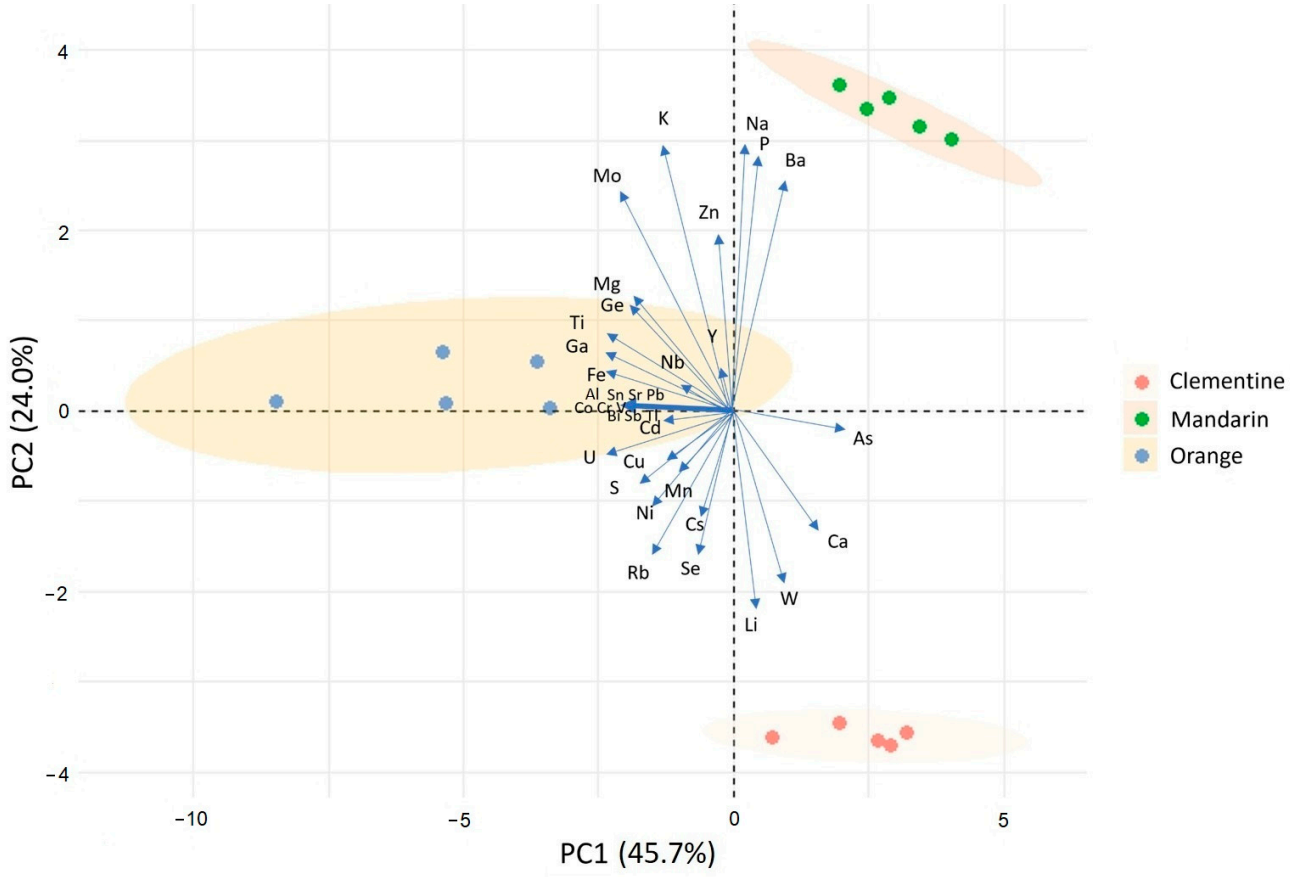


Figure 6. Principal component analysis (PCA) biplot of chemical elements found in clementine, mandarin, and orange peels. The plot shows the first two principal components (PC1 and PC2), which explain 70% of the total variation.

4. Conclusions

Based on approximate chemical analysis, clementine, mandarin, and orange peels can be classified as sources with low fat (0.95–1.12%), ash (1.00–1.17%), and protein (2.1–3.2%) content, and high moisture (74.4–74.7%), fibre (56.8–65.0%), and sugar (31.8–56.3%) content. Regarding fatty acids, polyunsaturated fatty acids (PUFAs) predominate in citrus peel, with contents of 51.8–59.6%. Linoleic and linolenic acids are present in the highest amounts,

particularly in clementine peels, at 30% and 25% respectively. Among monounsaturated fatty acids (MUFAs), oleic acid, the most important, was found at 8.0–17.7%, depending on the citrus peel. Palmitic acid, a saturated fatty acid (SFA), predominated with amounts of 17.6–19.9%, depending on the citrus peel. Nutritional indices, including the ratio of PUFA to SFA (1.94–2.30), MUFA to SFA (0.39–0.84), IA (0.34–0.47), IT (0.20–0.24), and HH (2.91–3.13), indicate that all peels analysed can make a significant contribution to cardiovascular health, making them good functional ingredients. Multi-element analysis showed that elements are unevenly distributed among citrus peels. The contribution of K as an essential macro element is the highest, followed by Ca > Mg > S > P > Na. Essential trace elements are distributed as Fe > Zn > Mn > Cu > Cr > Mo > Co > Se. Among non-essential elements (Al, As, Ba, Bi, Cd, Cs, Li, Ni, Pb, Rb, Sb, Sn, Sr, Ti, Tl, U, V, and Y), Al and Sr predominated, which did not show adverse effects on human health. However, the values of As were higher, which means it can be toxic according to the target hazard quotient (THQ). Among elements that rarely occur in food, and that are first detected for clementine, mandarin, and orange peels, such as Ga, Ge, Nb, V, W, and Y, the quantities were: W (11–79 μg/kg) > V (29–40 μg/kg) > Nb (10–11 μg/kg) and Ga (8–11 μg/kg) > Y (8 μg/kg) > Ge (2–5 μg/kg), depending on the citrus peel. Although clementine, mandarin, and orange peels have a nutrient-dense composition, their monitoring must be ensured before inclusion in the common diet, particularly regarding non-essential elements, as for most of them the reference doses are not established and they could be harmful to human health.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/foods15040781/s1, Table S1: Instrumental conditions of the used mass spectrometer and data acquisition parameters for the determination of selected elements; Table S2: Measured and certified element concentrations in the Citrus leaves certified reference material (NCS ZC73018). Table S3a: Results of the ANOVA test for the proximate chemical analysis of clementine, mandarin, and orange peels; Table S3b: Results of the Kruskal–Wallis test for proximate chemical analysis of clementine, mandarin, and orange peels; Table S4: Results of multi-element analysis of clementine, mandarin, and orange peels obtained by ICP-QQQ; Table S5: Loading profiles derived from principal component analysis (PCA) of the essential and non-essential elements found in clementine, mandarin, and orange peel.

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