

PHOSPHORUS AND IRON CONTENT IN APPLES IN DIFFERENT SALES CHANNELS

Marko PETEK¹, Matilda POVODNIK², Tomislav KARAŽIJA²,
Mihaela ŠATVAR VRBANČIĆ², Mile MARKOSKI³, Tomaš Lošak⁴, Goran FRUK⁵

¹University of Zagreb, Faculty of Agriculture, Department of Plant Nutrition,
Svetošimunska cesta 25, Zagreb, Croatia

²University of Zagreb, Faculty of Agriculture, Svetošimunska cesta 25, Zagreb, Croatia

³Ss. Cyril and Methodius University in Skopje, Str. 16-ta Makedonska brigada 3,
Skopje, Macedonia

⁴Mendel University in Brno, Faculty of Regional Development and International Studies,
trída Generála Píky 2005/7, Brno, Czech Republic

⁵University of Zagreb, Faculty of Agriculture, Svetošimunska cesta 25, Zagreb, Croatia

Corresponding author email: tkarazija@agr.hr

Abstract

*Phosphorus and iron are essential elements that are necessary for various functions of plants, but also for humans. The apple, *Malus × domestica* Borkh., is one of the most consumed fruits in the world, also in Croatia. Since the mentioned elements influence the growth and development of the plant and also have certain health effects on humans, the presence of these elements in apples on the Zagreb market should be investigated. After collecting and sampling the apples, the phosphorus content was determined by spectrophotometry and the iron content by atomic absorption spectrometry. Apples from retail chains statistically have the highest average phosphorus content in dry matter (0.14 % P DW), while apples from organic products stores statistically have the highest phosphorus content in fresh weight (27.29 mg P/100 g fresh weight). As for iron, the statistically highest average content in both dry matter and fresh matter was found in apples from retail chains (15.99 mg Fe/kg DM and 0.261 mg Fe/100 g fresh weight). These results could be the consequences of conventional agriculture.*

Key words: fruit quality, *Malus × domestica* Borkh., market distribution, minerals, nutritional value.

INTRODUCTION

Phosphorus is a vital macronutrient essential for energy metabolism in all living organisms (Vukadinović and Vukadinović, 2011). As a biogenic element, it is crucial for normal plant growth and development, playing a fundamental role in various biochemical processes, including photosynthesis, respiration, energy storage and transport, cell division, cell enlargement, and nitrogen fixation. Additionally, phosphorus is essential for seed germination, as well as the development of roots, shoots, and flowers (Muindi, 2019). Holford (1997) emphasizes that phosphorus is the most critical nutrient, after nitrogen, limiting agricultural productivity in many regions worldwide.

Inorganic phosphorus exists in the soil in various mineral forms, bound to adsorption complexes, and is present at very low

concentrations in the soil solution (Čoga and Slunjski, 2018). These low concentrations result from the rapid transformation of phosphate ions into less bioavailable forms, leading to phosphorus fixation. The availability of phosphorus is strongly influenced by soil pH and the saturation of the soil adsorption complex with bases (Čoga and Slunjski, 2018). At low pH, phosphorus forms insoluble compounds with iron and aluminum, while at near-neutral pH, it forms more soluble compounds with calcium and magnesium. At high pH, it again becomes insoluble due to the formation of calcium phosphate complexes (Muindi, 2019).

As the second most important macronutrient, phosphorus directly or indirectly regulates all biological processes within plants (Raghothama, 2005) and is crucial for growth and productivity (Malhotra et al., 2018). It significantly influences flowering and fruit

ripening (Muindi, 2019), and its deficiency can delay maturation, leading to postponed harvests and reduced fruit quality (Johnston and Steen, 2000). Furthermore, phosphorus is a key structural component of cellular membranes (Johnston and Steen, 2000) and plays a central role in adenosine triphosphate (ATP) synthesis, which serves as the primary energy carrier in biochemical processes (Muindi, 2019). Additionally, it is an essential constituent of nucleic acids, coenzymes, nucleotides, phosphoproteins, phospholipids, and sugar phosphates. Phosphorus is also integral to protein and vitamin biosynthesis, is present in key enzymes (Johnston and Steen, 2000), and is indispensable for the synthesis of nucleic acids and biological membranes (Lambers, 2021). Several studies underscore its critical role in photosynthesis (Johnston and Steen, 2000; Lambers, 2021; Muindi, 2019) and plant respiration (Muindi, 2019).

Iron, another essential element, is found in the soil in various soluble forms, including Fe^{2+} , Fe^{3+} , and FeOH^{2+} (Vukadinović and Vukadinović, 2011; Gluhić, 2013). According to Čoga and Slunjski (2018), Fe^{2+} is moderately mobile and exists in an exchangeable form within the soil adsorption complex, whereas Fe^{3+} is more tightly bound and largely immobile.

As a micronutrient, iron is indispensable for various metabolic pathways, including chlorophyll synthesis, photosynthesis, and respiration (Ning et al., 2023). It is also involved in protein synthesis, DNA replication, and biological nitrogen fixation, highlighting its importance for plant physiological functions. Plants primarily absorb iron in the form of Fe^{2+} and Fe^{3+} ions or as chelated complexes (Vukadinović and Vukadinović, 2011). Although iron is required in smaller quantities compared to macronutrients, it plays a crucial role in fruit quality, particularly in influencing the fresh-eating attributes of produce (Nour et al., 2010).

Iron deficiency in plants manifests as chlorosis, leaf shrinkage, and stunted growth, ultimately compromising normal development and reducing fruit quality and marketable yield (Ning et al., 2023). Furthermore, iron metabolism has been closely linked to the nutritional quality of plant-based food products (Briat et al., 2007), underscoring its

significance in agricultural and human nutrition.

The aim of this study was to determine the phosphorus and iron content in apples from three different sales channels in the city of Zagreb (Croatia).

MATERIALS AND METHODS

Apple fruits sampling was conducted on October 23, 2023, in the Zagreb to analyze phosphorus and iron content. Samples were collected from three different types of sales channels, with three separate locations for each channel:

- Markets (M): Savica (M1), Kvatrić (M2), and Dolac (M3)
- Retail chains (RC): Konzum (RC1), Eurospin (RC2), and Plodine (RC3)
- Organic product stores (OPS): bio & bio (OPS1), Spar Natur Pur (OPS2), and Priroda i društvo (OPS3).

Each sampling was performed in triplicate.

Label information at the sales points provided insights into the cultivation methods of the apples. Since apple samples from retail chains were not labeled as organic, they were assumed to be conventionally grown with the use of mineral fertilizers. Meanwhile, verbal inquiries with market vendors did not yield any details regarding fertilization practices. However, all samples from organic product stores were confirmed to be organically cultivated, as these stores exclusively sell certified organic products.

After collection, the average apple samples were sent to the analytical laboratory of the Department of Plant Nutrition at the Faculty of Agriculture, University of Zagreb, for chemical analysis. The fruits were peeled, sliced, and prepared for drying. They were dried at 105°C , then ground and homogenized. The samples were digested using concentrated nitric acid (HNO_3) and perchloric acid (HClO_4) in a microwave oven. Phosphorus content was determined through spectrophotometry, while iron content was analyzed using atomic absorption spectrometry (AOAC, 2023). Dry matter was measured gravimetrically by drying to a constant mass.

For statistical analysis, variance analysis (ANOVA) was applied using the SAS System

for Windows, version 9.1 (SAS Institute Inc.). The Tukey test (SAS, 2002-2003) was used to determine significant differences in the results.

RESULTS AND DISCUSSIONS

Table 1 shows the percentage of dry matter (% DM) in apples depending on the different distribution channels and points of sale. The apples from the Spar Natur Pur organic store (OPS2) have the statistically highest percentage of dry matter at 25.26%, while the apples from the Konzum retail chain (RC1) have the statistically lowest percentage at 15.52%. Table 1 also shows the percentage of dry matter (% DM) in apples sold through three different sales channels. This shows that apples from organic products stores (OPS) statistically have the highest dry matter content at 21.63%, apples from markets have a lower content of 17.11%, while apples from retail chains have the statistically lowest dry matter content at 16.52%.

Table 1. Dry matter (% DM) content determined in apple samples collected from, markets, retail chains and organic products stores

Sales channels		% dry matter			
Markets (M)	M1	15.69	e	17.11	b
	M2	17.31	d		
	M3	18.34	cd		
Retail chains (RC)	RC1	15.52	e	16.52	b
	RC2	18.24	c		
	RC3	15.79	e		
Organic products stores (OPS)	OPS1	18.40	c	21.63	a
	OPS2	25.26	a		
	OPS3	21.22	b		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

Table 2 presents the phosphorus content in the dry matter of apples across different sales channels. The highest statistically significant phosphorus concentration was observed in apples from the Plodine retail chain (RC3), measuring 0.16% P. Conversely, the lowest statistically significant phosphorus concentration, recorded at 0.11% P, was found in apples from the Kvatrić market (M2). On average, apples obtained from retail chains exhibited the highest phosphorus content at 0.14 % P, while the lowest average phosphorus

concentration was detected in apples from markets, at 0.12 % P (Table 2).

Table 2. Phosphorus content in dry matter of apple determined in samples collected from, markets, retail chains and organic products stores

Sales channels		% P in dry matter			
Markets (M)	M1	0.12	de	0.12	c
	M2	0.11	e		
	M3	0.14	b		
Retail chains (RC)	RC1	0.14	bc	0.14	a
	RC2	0.13	bc		
	RC3	0.16	a		
Organic products stores (OPS)	OPS1	0.14	b	0.13	b
	OPS2	0.13	cd		
	OPS3	0.12	cd		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

Table 3 illustrates the phosphorus content (mg P per 100 g in fresh apple matter) across different sales channels. The highest statistically significant phosphorus concentration was recorded in apples from the Spar Natur Pur organic products store (OPS2), measuring 32.09 mg P/100 g in fresh matter. In contrast, the lowest statistically significant phosphorus concentration was found in apples from the Savica market (M1), with a value of 18.19 mg P/100 g in fresh matter. On average (table 3), organic products stores exhibited the highest phosphorus content at 27.97 mg P/ 100 g in fresh matter, whereas markets had the lowest average phosphorus concentration at 21.21 mg P/100 g in fresh matter.

Table 3. Phosphorus content in fresh matter of apple determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg P/100 g in fresh matter			
Markets (M)	M1	18.19	f	21.12	c
	M2	19.21	f		
	M3	25.95	bc		
Retail chains (RC)	RC1	21.01	e	23.05	b
	RC2	23.69	d		
	RC3	24.46	cd		
Organic products stores (OPS)	OPS1	25.46	bc	27.97	a
	OPS2	32.09	a		
	OPS3	26.36	b		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

The analysis of iron content in the dry matter of apples revealed a range of 10.52 to 22.87 mg Fe/kg in dry matter (Table 4). The highest statistically significant iron concentration per kilogram of dry matter was recorded in apples from the Plodine retail chain (RC3), whereas the lowest concentration was detected in apples from the Spar Natur Pur organic products store (OPS2). Notably, the three highest iron concentrations were distributed across all three sales channels, with the Plodine retail chain exhibiting the highest value at 22.87 mg Fe/kg in dry matter, followed by the bio&bio organic products store (OPS1) with 15.44 mg Fe/kg in dry matter, and the Savica market (M1) with 15.40 mg Fe/kg in dry matter. On average, the organic products stores exhibited the lowest iron content, with a mean value of 12.17 mg Fe/kg in dry matter, while the retail chains had the highest average iron concentration at 15.99 mg Fe/kg in dry matter (Table 4).

Table 4. Iron content in dry matter of apple determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Fe/kg in dry matter			
Markets (M)	M1	15.40	b	14.11	b
	M2	12.30	de		
	M3	14.63	bc		
Retail chains (RC)	RC1	13.60	cd	15.99	a
	RC2	11.50	ef		
	RC3	22.87	a		
Organic products stores (OPS)	OPS1	15.44	b	12.17	c
	OPS2	10.52	f		
	OPS3	10.55	f		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

The iron content in fresh apple matter was found to range from 0.211 to 0.361 mg Fe/100 g in fresh matter (Table 5). The highest statistically significant iron concentration was observed in apples from the Plodine retail chain (RC3), whereas the lowest statistically significant concentration, measuring 0.211 mg Fe/100 g in fresh matter, was recorded at three different locations: Kvatrić market (T2), the Konzum retail chain (RC1), and the Eurospin retail chain (RC2). On average, apples from retail chains exhibited the highest iron content at 0.261 mg Fe/100 g in fresh matter, while those from markets had the lowest average iron

concentration at 0.24 mg Fe/100 g in fresh matter (Table 5).

Table 5. Iron content in fresh matter of apple determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Fe/100 g in fresh matter			
Markets (M)	M1	0.241	c	0.240	c
	M2	0.212	d		
	M3	0.268	b		
Retail chains (RC)	RC1	0.211	d	0.261	a
	RC2	0.210	d		
	RC3	0.361	a		
Organic products stores (OPS)	OPS1	0.284	b	0.258	b
	OPS2	0.266	b		
	OPS3	0.224	cd		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

A study conducted in Romania by Campeanu et al. (2009) reported that the phosphorus content in apple dry matter ranged between 0.351 and 0.526% P in dry matter, which is higher than the values obtained in this study in Croatia, where phosphorus levels ranged from 0.11 to 0.16% P in dry matter. Conversely, findings from Sachini et al. (2020) indicated that the phosphorus content in fresh apple pulp in Brazil varied between 15.58 and 24.26 mg P/100 g in fresh matter, whereas in Croatia, the highest recorded phosphorus concentration in organic products stores was 32.09 mg P/100 g in fresh matter.

Significant variations were also observed in iron content across different studies. Gogoasa et al. (2015) reported that domestic apple varieties in Romania contained iron levels between 3.84 and 6.02 mg Fe/kg in dry matter, whereas in this study, iron concentrations were significantly higher, ranging from 10.52 to 22.87 mg Fe/kg in dry matter. The lower values observed in Romania may be attributed to the fact that the apples analyzed originated from regions with minimal anthropogenic influence. A study conducted in Italy on the 'Golden Delicious' variety also examined in the present study found an iron content of 10.25 mg Fe/kg in dry matter, which is slightly lower than the values recorded in Croatia, where the range was 11.50 to 22.87 mg Fe/kg in dry matter.

Furthermore, a study by Veo et al. (2022) analyzed the iron content in twelve apple varieties from retail chains in the Bismarck region, reporting values between 0.11 and 0.15 mg Fe/100 g in fresh matter. This is slightly lower than the iron content measured in retail chain apples in the present study, where values ranged from 0.210 to 0.361 mg Fe/100 g in fresh matter. Among the varieties collected in Bismarck, the 'Gala' variety exhibited the lowest iron content at 0.11 mg Fe/100 g in fresh matter. In the present study, iron content for the same variety was measured at 0.266 and 0.224 mg Fe/100 g in fresh matter, aligning more closely with the results of the Bismarck study, despite the samples here being collected from organic products stores.

The comparison of phosphorus and iron content across various studies suggests that multiple factors, including apple variety, growing region, cultivation practices, and analytical methods, can influence the final results.

Regarding dietary intake, the recommended daily phosphorus intake for adults is approximately 1000 mg P/day (Goyal and Jialal, 2019). The highest contribution to daily phosphorus intake was found in apples from the organic products stores, accounting for 2.80% of the recommended daily phosphorus requirement.

For iron, the daily requirement is 10 mg Fe for males over 10 years and females over 50 years, while women aged 11-50 require 15-20 mg Fe/day (Hui, 2006). Apples collected from the retail chains contributed the highest to daily iron intake, providing approximately 2.61% of the recommended daily intake for men and 1.74% for women.

CONCLUSIONS

It was found that apples from retail chains often have a higher concentration of phosphorus than apples from local markets, which can be linked to the more intensive use of phosphate fertilizers in conventional agriculture. The range of phosphorus content in the dry matter ranged from 0.11 to 0.16% P in dry matter and from 18.19 to 32.09 mg P/100 g in fresh matter at the retail chains. In contrast, there were also fluctuations in the iron content, with apples from retail chains having a higher iron content

than those from organic products stores and local markets. The values determined in the dry matter were between 10.52 and 22.87 mg Fe/kg in dry matter and in the fresh matter between 0.211 and 0.361 mg Fe/100 g in fresh matter.

The results of this study contribute to a better understanding of how different cultivation and distribution factors can influence the content of important nutrients in apples.

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