

CONTENT OF MICROELEMENTS IN FRENCH BEAN PODS FROM DIFFERENT CULTIVATIONS

Marko PETEK¹, Ema KLARIĆ², Sanja FABEK UHER²,
Antun ŠOKEC², Szilvia VERES³, Šic Žlabur JANA²

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

³University of Debrecen, Egyetem tér 1, Debrecen, Hungary

Corresponding author email: sfabek@agr.hr

Abstract

The aim of this work was to determine how the cultivation method affects the microelements content of the French bean (*Phaseolus vulgaris* L.) pods. The pod samples were collected in the city of Zagreb at three markets, three retail chains and three stores selling organic products. The concentrations of iron, zinc, manganese and copper were determined using an atomic absorption spectrometer. The value of the dry matter in the pods was between 6.74 and 12.54%. The proportion of microelements in the dry matter of the pods (mg/kg ST) was Fe 49.86-188.9, Zn 23.43-43.47, Mn 2.53-42.3, Cu 6.57-9.74, and in the fresh matter (mg/100 g fresh matter) Fe 0.49-1.96, Zn 0.19-0.42, Mn 0.03-0.32 and Cu 0.05-0.11. According to the Regulation on the provision of food information to consumers, it can be concluded that the consumption of 100 g of the studied french beans tested covers 4.21-8.0% of the daily human requirement of iron, 2.5-3.8% of the daily requirement of zinc, 4.0-13.0% of the daily requirement of manganese and 7.0-8.0% of the daily requirement of copper.

Key words: copper, iron, manganese, *Phaseolus vulgaris* L., zinc.

INTRODUCTION

A French bean pods are the fruits of *Phaseolus vulgaris* L., commonly known as the bean or common bean or filed bean, an annual herbaceous species within the legume family (Fabaceae) (Carović-Stanko et al., 2022). French bean pods are typically preserved through methods such as sterilization or freezing to ensure availability throughout the year, although they may also be consumed fresh (Lešić et al., 2016; Carović-Stanko et al., 2022). Microelements are essential nutrients required by plants in trace amounts, yet they play a critical role in plant growth and development, comparable to that of macroelements which plants need in larger amounts. Despite their low concentrations in plant tissues, they are indispensable for various physiological and biochemical processes.

Iron (Fe) is predominantly bound within plant tissues, with approximately 80-90% existing in tightly bound forms, making it moderately to poorly mobile. Its movement within plants is hindered when complexed with

hydroxycarboxylic acids, amino acids, phenols, thiols, or polysaccharides, particularly in the presence of Ca(HCO₃) (Vukadinović and Vukadinović, 2011). Structurally, iron is an integral component of numerous prosthetic groups in enzymes, including cytochromes, peroxidases, and catalases. Cytochromes, which share structural similarities with chlorophyll, contain an iron atom within the porphyrin core and function as coenzymes in electron transport (Lazarević and Poljak, 2019). Additionally, iron is crucial in oxidoreduction reactions, particularly within Fe-S proteins such as ferredoxin, which facilitates the interconversion of Fe²⁺ and Fe³⁺ within photosystem I (Vukadinović et al., 2014). Iron also regulates chlorophyll synthesis and photosynthesis by modulating the concentration of α -aminolevulinic acid (ALA), a key precursor of heme and chlorophyll (Bahat and Stepinac, 2011).

Zinc (Zn), although required in trace amounts, is essential for plant physiological processes. It is the only metal involved in all major enzyme classes, including oxidoreductases, transferases, hydrolases, lyases, isomerases, and ligases

(Sadeghzadeh, 2013). Zinc is necessary for the synthesis of RNA polymerase, thereby influencing DNA and RNA synthesis as well as overall protein synthesis. It also protects ribosomal RNA from degradation by ribonuclease enzymes (Rudani et al., 2018). Furthermore, zinc is vital for auxin metabolism, particularly in the biosynthesis of indoleacetic acid (IAA), an essential plant growth hormone. It plays a crucial role in the synthesis of tryptophan, a precursor of IAA (Lazarević and Poljak, 2019; Hafeez et al., 2013). Manganese (Mn) is an essential element involved in a variety of biochemical and oxidation-reduction processes within plants. It serves as an enzymatic cofactor, particularly for enolase and carboxylase, and is integral to the Krebs cycle, where it activates decarboxylase and dehydrogenase enzymes. Manganese is indispensable for photosynthesis and nitrogen metabolism, acting as a cofactor in photosystem II electron transport. It also plays a pivotal role in water photolysis, a process essential for oxygen evolution during photosynthesis (Vukadinović and Vukadinović, 2011; Lazarević and Poljak, 2019). Copper (Cu) is another essential microelement involved in plant physiological and biochemical processes. It functions as a cofactor in numerous enzymes responsible for redox reactions, given its ability to reversibly transition between Cu^+ and Cu^{2+} oxidation states (Lazarević and Poljak, 2019). Copper is crucial in cell wall metabolism, protein metabolism, photosynthetic electron transport, hormone signaling, oxidative stress responses, and mitochondrial respiration. It also serves as an ethylene sensor, with its most critical function being electron transfer in mitochondrial and chloroplast reactions (Pradeep and Aishwarya, 2023; Chen et al., 2022; Miljković et al., 2018; La Torre et al., 2018). Copper is a key component of enzymes such as ribulose diphosphate carboxylase and cytochrome c oxidase, both of which are essential for photosynthesis and cellular respiration. Its deficiency leads to impaired chlorophyll synthesis, thylakoid membrane formation, and overall photosynthetic efficiency, resulting in chlorosis as a primary symptom (Rusjan, 2012). The objective of this study is to determine the microelement content in French bean pods purchased from different sales channels, including markets, retail chains, and organic products stores. The findings will be analyzed to

assess whether the cultivation method and point of purchase influence the microelement composition of the beans.

MATERIALS AND METHODS

Sampling of French bean pods was conducted on October 17, 2022, in Zagreb to determine phosphorus and iron concentrations. Samples were collected from three distinct sales channels, with three separate sampling locations within each channel:

Markets (M): Dolac (M1), Kvatrić (M2), and Voćarna Agrovir (M3)

Retail Chains (RC): Eurospin (RC1), Kaufland (RC2), and Spar (RC3)

Organic Product Stores (OPS): Garden (OPS1), bio & bio (OPS2), and Mrkvica (OPS3)

Each sampling was conducted in triplicate to ensure reliability.

Label declarations at sales points provided insights into the cultivation methods of the sampled French bean pods. As the samples from retail chains were not labeled as organic, they were presumed to be conventionally cultivated using mineral fertilizers. Verbal inquiries with market vendors did not yield specific information regarding fertilization practices. In contrast, all samples obtained from organic product stores were confirmed to be organically grown, as these stores exclusively sell certified organic products.

Following collection, composite samples were transported to the analytical laboratory of the Department of Plant Nutrition at the Faculty of Agriculture, University of Zagreb, for chemical analysis. The French bean pods were processed by peeling, slicing, and drying at 105°C . The dried samples were then ground, homogenized, and digested using concentrated nitric acid (HNO_3) and perchloric acid (HClO_4) in a microwave-assisted digestion system. Iron, zinc, manganese and copper concentration was determined via atomic absorption spectrometry (AOAC, 2023). Dry matter content was assessed gravimetrically by drying samples to a constant mass.

Statistical analysis was performed using analysis of variance (ANOVA) with the SAS System for Windows, version 9.1 (SAS Institute Inc.). The Tukey test (SAS, 2002-2003) was employed to assess significant differences among the results.

RESULTS AND DISCUSSIONS

Table 1 presents the dry matter content of French bean pods samples analyzed according to their sales channel. The dry matter content in French bean pods obtained from market samples ranged from 8.28 to 12.54%, while samples from retail chains exhibited dry matter content values between 6.74 and 10.50%. In contrast, French bean pods from organic products stores showed dry matter contents ranging from 7.83 to 10.39%. The lowest dry matter content was observed in French bean pods sampled from the 'Spar' retail chain (6.74% dry matter), whereas the highest value was recorded in French bean pods from the 'Dolac' market (12.54% dry matter). Statistically, the highest dry matter content was found in the samples from the 'Dolac' market, while the lowest values were observed in French bean pods from the retail chains 'Spar' (6.74% dry matter) and 'Kaufland' (7.31% dry matter).

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

Sales channels		% dry matter			
Markets (M)	M1	12.54	a	10.38	a
	M2	10.32	b		
	M3	8.28	d		
Retail chains (RC)	RC1	10.50	b	8.18	b
	RC2	7.31	ef		
	RC3	6.74	f		
Organic products stores (OPS)	OPS1	10.39	b	9.31	ab
	OPS2	7.83	de		
	OPS3	9.71	c		
Different letters represent significantly different values according to Tukey's test, $p \leq 0.05$. The non-letter values are not significantly different.					

The average iron content (mg Fe/kg dry matter) in French bean pods sampled from markets and retail chains did not exhibit a statistically significant difference. However, the average iron content in organic products stores was statistically higher (Table 2). The iron content in the dry matter of French bean pods across the different sales channels ranged from 49.86 to 188.90 mg Fe/kg dry matter. The highest statistically significant iron content was recorded in samples from the 'Garden' organic products store (188.90 mg Fe/kg dry matter), while the lowest value was observed in French

bean pods from the 'Kvatrić' market (49.86 mg Fe/kg dry matter).

Table 2. Iron content in dry matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Fe/kg dry matter			
Markets (M)	M1	74.14	c	63.42	b
	M2	49.86	d		
	M3	66.25	c		
Retail chains (RC)	RC1	70.58	c	72.94	b
	RC2	75.25	c		
	RC3	73.00	c		
Organic products stores (OPS)	OPS1	188.90	a	115.82	a
	OPS2	70.23	c		
	OPS3	88.33	b		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

Iron content in fresh French bean pods sampled from organic products stores was consistently higher than that in French bean pods from markets and retail chains (Table 3).

Table 3. Iron content in fresh matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Fe/100 g in fresh matter			
Markets (M)	M1	0.93	b	0.66	b
	M2	0.51	d		
	M3	0.55	d		
Retail chains (RC)	RC1	0.74	c	0.59	b
	RC2	0.55	d		
	RC3	0.49	d		
Organic products stores (OPS)	OPS1	1.96	a	1.12	a
	OPS2	0.55	d		
	OPS3	0.86	b		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

The average iron content in fresh French bean pods was statistically highest in organic products stores. Iron content in fresh French bean pods ranged from 0.49 to 1.96 mg Fe/100 g. The highest iron content in fresh green beans was found in samples from the 'Garden' organic food store (1.96 mg Fe/100 g), while the lowest was recorded in green beans from the 'Spar' retail chain (0.49 mg Fe/100 g). Statistically, the 'Garden' organic products store displayed the highest iron concentration in fresh French bean pods.

The average zinc content in the dry matter of French bean pods was highest in organic products stores, which also exhibited the statistically significant highest mean zinc concentrations. Conversely, the lowest average zinc content in dry matter was observed in market samples (Table 4). The highest zinc concentration in the dry matter of field beans was recorded in the organic store 'Mrkvica' (43.47 mg Zn/kg dry matter), while the lowest was found in the 'Voćarna' market (23.43 mg Zn/kg dry matter). Statistically significant higher zinc concentrations in the dry matter were identified in the organic products stores 'Mrkvica', 'bio & bio', and 'Garden', as well as in the retail chain 'Kaufland'.

Table 4. Zinc content in dry matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Zn/kg dry matter			
Markets (M)	M1	32.51	bc	27.3	b
	M2	25.96	de		
	M3	23.43	f		
Retail chains (RC)	RC1	25.42	de	31.86	b
	RC2	39.65	a		
	RC3	30.51	cd		
Organic products stores (OPS)	OPS1	37.67	ab	41.02	a
	OPS2	41.90	a		
	OPS3	43.47	a		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different					

The zinc content in fresh French bean pods from retail stores ranged from 0.19 to 0.42 mg Zn/100 g fresh weight (Table 5).

Table 5. Zinc content in fresh matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Zn/100 g in fresh matter			
Markets (M)	M1	0.41	A	0.29	b
	M2	0.27	C		
	M3	0.19	D		
Retail chains (RC)	RC1	0.27	C	0.25	b
	RC2	0.29	Bc		
	RC3	0.20	D		
Organic products stores (OPS)	OPS1	0.39	A	0.38	a
	OPS2	0.33	B		
	OPS3	0.42	A		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

The highest zinc concentration in fresh weight was determined in the organic products store 'Mrkvica', while the lowest was observed in the 'Voćarna' market. Statistically, the highest zinc values in fresh weight were found in the organic products stores 'Mrkvica' (0.42 mg Zn/100 g fresh weight) and 'Garden' (0.39 mg Zn/100 g fresh weight), as well as in the 'Dolac' market (0.41 mg Zn/100 g fresh weight).

The average manganese content in the dry matter of French bean pods, by sales channels, was highest in organic product stores, followed by retail chains and markets. Statistically, the highest mean manganese content in dry matter was observed in both retail chains and organic product stores. Manganese concentrations in the dry matter of French bean pods ranged from 2.53 to 42.3 mg Mn/kg dry matter (Table 6). The highest manganese content in dry matter was recorded in the 'Kaufland' retail chain (42.3 mg Mn/kg dry matter), while the lowest was found in the 'Kvatrić' market (2.53 mg Mn/kg dry matter). The statistically highest value was observed in the 'Kaufland' retail chain (42.3 mg Mn/kg dry matter), with additional significant values recorded in the 'bio & bio' (33.48 mg Mn/kg dry matter) and 'Mrkvica' (32.85 mg Mn/kg dry matter) organic products stores, as well as in the 'Spar' retail chain (32.94 mg Mn/kg dry matter).

Table 6. Manganese content in dry matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Mn/kg dry matter			
Markets (M)	M1	6.29	Cd	8.14	b
	M2	2.53	D		
	M3	15.61	Bc		
Retail chains (RC)	RC1	5.20	Cd	26.81	a
	RC2	42.30	A		
	RC3	32.94	A		
Organic products stores (OPS)	OPS1	18.94	Bc	28.42	a
	OPS2	33.48	a		
	OPS3	32.85	a		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different					

In fresh French bean pods, the highest average manganese content across distribution channels was observed in organic products stores, while the lowest was found in markets. Statistically, the highest average manganese content in fresh French bean pods was detected in organic

products stores and retail chains. The manganese content in fresh produce ranged from 0.03 to 0.32 mg Mn/100 g fresh weight (Table 7). The highest manganese concentration in fresh French bean pods was identified in the ‘Mrkvica’ organic products store, while the lowest was observed in the ‘Kvatrić’ market. Statistically, the highest manganese values in fresh French bean pods were found in the ‘Mrkvica’ organic products store (0.32 mg Mn/100 g fresh weight), followed by the ‘Kaufland’ retail chain (0.31 mg Mn/100 g fresh weight) and the ‘bio & bio’ organic food store (0.26 mg Mn/100 g fresh weight). The lowest statistically significant value was recorded in the ‘Kvatrić’ market, with a manganese content of 0.03 mg Mn/100 g fresh weight.

Table 7. Manganese content in fresh matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Mn/100 g in fresh matter			
Markets (M)	M1	0.08	de	0.08	b
	M2	0.03	e		
	M3	0.13	cd		
Retail chains (RC)	RC1	0.05	de	0.19	a
	RC2	0.31	a		
	RC3	0.22	b		
Organic products stores (OPS)	OPS1	0.20	bc	0.26	a
	OPS2	0.26	ab		
	OPS3	0.32	a		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

The average copper content in the dry matter of French bean pods is highest in retail chains and lowest in markets. The copper concentrations in the dry matter of field beans ranged from 6.57 to 9.74 mg Cu/kg dry matter (Table 8). The highest copper content was observed in the ‘Eurospin’ retail chain, while the lowest value was found in the ‘Mrkvica’ organic products store. Statistically, the highest copper content in the dry matter of French bean pods was recorded in the ‘Eurospin’ retail chain, with additional significant concentrations found in the ‘bio & bio’, ‘Kaufland’, ‘Garden’, ‘Dolac’, ‘Kvatrić’, and ‘Spar’.

In contrast, the average copper content in fresh French bean pods was similarly high in organic products stores and markets, but comparatively lower in retail chains. Copper concentrations in the fresh matter of French bean pods ranged

from 0.05 to 0.11 mg Cu/100 g fresh weight (Table 9). The highest copper content was detected in the ‘Dolac’ market, while the lowest was found in the ‘Spar’ retail chain. Statistically, the highest values were recorded in the ‘Dolac’ market (0.11 mg Cu/100 g fresh weight), followed by the ‘Eurospin’ retail chain (0.10 mg Cu/100 g fresh weight) and the ‘Garden’ organic products store (0.09 mg Cu/100 g fresh weight).

Table 8. Copper content in dry matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Cu/kg dry matter			
Markets (M)	M1	8.58	abc	7.75	-
	M2	7.82	abc		
	M3	6.85	bc		
Retail chains (RC)	RC1	9.74	a	8.74	-
	RC2	9.12	abc		
	RC3	7.37	abc		
Organic products stores (OPS)	OPS1	8.81	abc	8.19	-
	OPS2	9.20	ab		
	OPS3	6.57	c		
Different letters represent significantly different values according to Tukey's test, p<0.05. The non-letter values are not significantly different.					

Vegetables represent a crucial component of a healthy diet due to their high content of carbohydrates, phytonutrients, fiber, vitamins, and minerals, serving as an essential source of nutritionally valuable elements. The dietary guidelines established by the World Health Organization (WHO) and the Food and Agriculture Organization (FAO) recommend a minimum daily intake of 400 g of fruits and vegetables to prevent nutrient deficiencies.

Table 9. Copper content in fresh matter of French bean pods determined in samples collected from, markets, retail chains and organic products stores

Sales channels		mg Cu/100 g in fresh matter			
Markets (M)	M1	0.11	a	0.08	-
	M2	0.08	bcd		
	M3	0.06	de		
Retail chains (RC)	RC1	0.10	ab	0.07	-
	RC2	0.07	de		
	RC3	0.05	e		
Organic products stores (OPS)	OPS1	0.09	abc	0.08	-
	OPS2	0.07	cde		
	OPS3	0.06	de		
Different letters represent significantly different values according to Tukey's test, p≤0.05. The non-letter values are not significantly different.					

Plants absorb minerals from the soil, water, and air, and thus the mineral composition of vegetables is influenced by various factors, including cultivation methods (organic versus conventional, which is closely associated with fertilization practices), environmental conditions, and environmental stresses such as salinity, drought, irrigation water quality, and extreme temperatures. Elevated concentrations of toxic elements in plants can interfere with the uptake of essential nutrients, leading to disruptions in physiological functions such as electron transfer, photosynthesis, respiration, metabolic and enzymatic processes, ultimately affecting plant growth and development (Popović-Djordjević et al., 2021). Same authors conducted a study on various types of organically and conventionally grown vegetables (cabbage, kohlrabi, Brussels sprouts, beetroot, carrots, potatoes, and onions) sourced from urban markets. Their findings revealed that the type of vegetable has a more pronounced effect on the mineral composition than the production method. In a similar research, Hunter et al. (2011) reported significantly higher concentrations of microelements in organically grown fruits, vegetables, French bean pods, and cereals. Furthermore, Czech et al. (2022) observed in their study on various species within the genus *Allium* that organically grown vegetables exhibited higher levels of minerals such as calcium, magnesium, iron, zinc, copper, and manganese, as well as bioactive compounds. This study concluded that the consumption of organically grown *Allium* vegetables confers a more favorable effect on human health. Additionally, Akbaba et al. (2012) found that in their study on *Phaseolus vulgaris* L. (beans), organically grown beans contained higher concentrations of essential elements including calcium, iron, manganese, phosphorus, zinc, chlorine, potassium, sodium, magnesium, and silicon, a finding that aligns with the results of the present study.

CONCLUSIONS

The highest dry matter content in pod samples was observed in the average sample by sales channels at the markets (10.38%). The highest average concentrations of iron, zinc, and manganese in both the dry and fresh mass of

French bean pods were found in organic products stores, with values of 115.82 mg Fe/kg dry matter (DM) and 1.12 mg Fe/100 g fresh mass, 41.02 mg Zn/kg DM and 0.38 mg Zn/100 g fresh mass, and 28.42 mg Mn/kg DM and 0.26 mg Mn/100 g fresh mass. The highest average copper content in dry matter was recorded in pods sampled from retail chains (8.74 mg Cu/kg DM). In terms of fresh matter, the highest average copper concentration was measured in samples from both markets and organic products stores, where it was 0.08 mg Cu/100 g fresh mass in each distribution channel.

When comparing these measured values with the recommended daily intake values outlined in the Regulation (EU) on Food Information to Consumers, it can be concluded that the consumption of 100 g of the tested French bean pods contributes to 4.21-8.0% of the daily human requirement for iron, 2.5-3.8% for zinc, 4.0-13.0% for manganese, and 7.0-8.0% for copper.

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