

ANTIOXIDANT CAPACITY AND SEASONAL MINERAL COMPOSITION VARIATION IN *ARONIA MELANOCARPA* FRUITS

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Abstract

Aronia melanocarpa fruits have been linked to a variety of health benefits due to their nutritional, antioxidant, antiviral, and anti-inflammatory properties. The main objective of this study was to identify the optimal harvest time for maximum nutritional antioxidant potential and nutritional mineral concentrations. Ten berry samples of 'Nero Eggert' *Aronia melanocarpa* variety were harvested twice per week over 5 weeks (August-September). *Aronia* berries harvested in early August contain high concentrations of dietary macronutrients: Ca (807.17 mg/kg), K (3,070.15 mg/kg), Mg (201.94 mg/kg), Na (116.77 mg/kg), dietary ultratrace elements: B (168.65 mg/kg) and Sr (1.14 mg/kg) and total flavonoid content (TFC - 1,722.87 mg CE/100 g). Berries harvested in early September contain high total polyphenol concentrations (TPC - 2,358.65 mg GAE/100 g), total antioxidant capacity (TAC - 41.58 mmol TE/ 100 g), total anthocyanin content (TA - 357.17 mg CGE/100 g) and ferric reducing antioxidant power (FRAP - 69.33 mmol Fe(II)/100 g), high concentrations of dietary micronutrients: Cr (0.39 mg/kg), Cu (1.53 mg/kg), Fe (110 mg/kg), Mn (9.2 mg/kg), Zn (108.32 mg/kg), which make them recommended for functional and personalized foods with high polyphenol content.

Key words: chokeberry, nutritional value, minerals, polyphenols.

INTRODUCTION

Due to its rich chemical composition, which varies based on a number of parameters including soil composition, fertilization, climate, berry ripeness, harvesting technique, and storage conditions, *Aronia melanocarpa* has attracted a lot of interest in the scientific world and food industry (Tolić et al., 2017). *Aronia melanocarpa* is a 2-3 m shrub (Jurendić and Šćetar, 2021) and one of four recognized species of the genus *Aronia* Medik, in the *Rosaceae* family, also known as black chokeberry (Mahoney et al., 2019).

Aronia berries, also known as chokeberries, are one of the greatest sources of polyphenols and anthocyanins in the plant kingdom, making them an ideal raw material for the development

of functional food. Their popularity stems from both their nutritional content and health-promoting properties (Denev et al., 2018). Research has shown that these compounds can have a meaningful beneficial impact on health through their antioxidative, anti-inflammatory, antiviral, anticancer, antiatherosclerosis, hypotensive, antiplatelet, and antidiabetic properties (Borowska and Brzóska, 2016). Being remarkably rich in anthocyanins, flavanols, proanthocyanins, and phenolic acids (King and Bolling, 2020), chokeberries' overall polyphenol content ranges from 1,022 mg/100 g fresh weight (fw) to 1,795 mg/100 g fw, with anthocyanins accounting for 284-686 mg/100 g fw (Denev et al., 2018). A study conducted by Xie et al. (2016) showed that after the consumption of 500 mg aronia extract, their

polyphenols were absorbed and extensively metabolized. Consuming the same quantity also has a beneficial impact on low-density lipoprotein cholesterol (LDL-C); a study on former smokers showed an 8% reduction in LDL-C after 12 weeks compared to the placebo group (Xie et al., 2017).

Aronia melanocarpa is also known for its complex mineral content in fruits, containing calcium, potassium, iron, molybdenum, manganese, phosphorus and iodine (Djuric et al., 2015). Very few information is published on aronia fruits and products (juice, filter bags for infusion and pomace) mineral content (Cindrić et al., 2017; Jurendić & Ščetar, 2021; King & Bolling, 2020; Kulling & Rawel, 2008; Sidor et al., 2019; Pieszka et al., 2015; Pavlovic et al., 2015).

The aim of this study was to determine how the harvest date impacts the antioxidant capacity of *Aronia melanocarpa* berries and their mineral composition.

MATERIALS AND METHODS

Ten samples of *Aronia melanocarpa* variety ‘Nero Eggert’ fruits were harvested twice per week during August and beginning of September in 2022 from plants located in the experimental orchard of the Integrated Fruit Growing Laboratory of the Faculty of Horticulture, University of Agronomic Sciences and Veterinary Medicine of Bucharest. All samples were frozen at -32°C until time of analysis. All data presented in this paper are for wet weight samples (fresh fruits).

Antioxidant capacity

The following parameters were measured:

- the total polyphenol content (TPC) - was measured using a modified Folin-Ciocalteu method and the results were expressed as milligrams of gallic acid equivalents/100 g fruit (mg GAE/100 g) (Predescu et al., 2016);
- the total flavonoid content (TFC) - was evaluated by aluminium chloride method and the results were expressed as milligrams catechin equivalent/100 g (mg CE/100 g) (Predescu et al., 2016);
- the total anthocyanin content (TA) - was determined by pH differential method and the results were expressed as mg cyanidin-3-

glucoside equivalents/100 g fruit (mg CGE/100 g) (Panico et al., 2009);

- the total antioxidant capacity (TAC) - was evaluated using 1,1-diphenyl-2-picrylhydrazyl (DPPH•) and the results were expressed as mmol Trolox equivalents/100 g fruit (mmol TE/100 g) (Predescu et al., 2016);
- a spectrophotometric method was used to estimate the ferric reducing antioxidant power (FRAP) and the results were expressed as mmol Fe(II) equivalents/100 g fruit (Predescu et al., 2016).

Mineral concentration

Aronia fruits were ground and 0.90 g to a maximum of 1.00 g of fruits were mixed with 8 ml of nitric acid 65% Suprapur Merck.

The samples were digested using a Speedwave Berghov microwave digestion oven for digestion (Table 1). After cooling, the samples were diluted with ultrapure water to the 50 ml flasks (sample solution).

Table1. Microwave digestion oven operating parameters

Parameter	Stage 1	Stage 2	Stage 3
Power (%)	50	50	40
Temperature °C	145	180	100
Execution time (min)	5	10	10

The samples solutions were analysed using an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) (Table 2).

Table 2. ICP-OES operating conditions

Parameter	Value
Frequency	27.12 MHz
Rf Power	1.5 kw
Argon Gas flow	14 L/min
Nebulizer Type	cyclonic
Stabilization Time	3-5 s
Number of Probes for each Measurement	3

The following micro and macro elements have been determined: Al 396.1 nm; B 208.9 nm, Ba 233.5 nm; Ca 393.9 nm; Cr 267.7 nm; Cu 224.7 nm; Fe 259.9 nm; K 769.8 nm; Mg 280.2 nm; Mn 257.6 nm; Na 589.5 nm; Ni 221.6 nm; Sr 421.5 nm; Zn 213.8 nm.

Statistical analysis

Statistical analysis was performed using MedCalc® Statistical Software version 22.006 (MedCalc Software Ltd, Ostend, Belgium; <https://www.medcalc.org>; 2024). Data normality was tested using the Shapiro-Wilk test and

Levene's test was used for testing equality of error variances. The post-hoc analysis was performed using Tukey-Kramer test in case of a significant one-way ANOVA analysis. When data was not normally distributed, the Kruskal-Wallis test was applied.

RESULTS AND DISCUSSIONS

Antioxidant capacity

The TPC, TFC, TA, TAC and FRAP for *Aronia melanocarpa* fruits during harvest are presented in Figures 1 to 5.

Total polyphenol content (TPC)

The variation of environment temperature influences the biosynthesis of plant tissues polyphenols (secondary metabolites) the process depending on the gene's activity responsible for phenolic compounds synthesis as a response to the increase in the accumulation of reactive oxygen species (ROS) within plant cells (Zagoskina et al., 2023). This explains the increase of TPC concentrations in aronia berries for the harvests from 17 and 31 August. On the other hand, as the fruits ripen, TPC concentration may decreases (Dobros et al., 2024) explaining the decrease observed for 23-27 August. Several authors have reported values between 1,022 mg GAE /100 g and 1,795 mg GAE/100 g (Denev et al., 2018) and up to 4,393.50 mg/100 g at their peak ripening stage (Yang et al., 2019). Engin & Mert (2020) reported a steady increase during August and mid-September followed by a decrease until the end of September for an aronia cultivar in Turkey. For the data in Figure 1, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.7586$, Levene's test $P=0.418$, one-way ANOVA $P<0.001$).

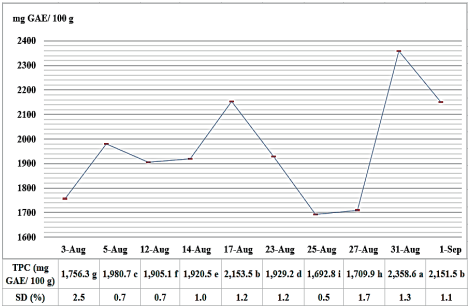


Figure 1. Variation of TPC (mg GAE/100 g) in *Aronia melanocarpa* fruit samples during harvest

Total flavonoid content (TFC)

Light is an important environmental factor in regulating the flavonoid accumulation in fruits, high exposure to sunlight regulating the flavonol biosynthetic gene MdFLS and several anthocyanin biosynthetic genes, including MdCHS, MdCHI, MdF3H, MdDFR1, leucoanthocyanidin dioxygenase (MdLDOX) and MdUFGT (Zoratti et al., 2014). Weather conditions and fruit positioning can explain the high TFC concentrations from August 17 and September 1st harvests. The oxidation of flavonoids to their corresponding semiquinones and quinones by oxidases such as polyphenol oxidases (PPO) and peroxidases (POD) during ripening (Pourcel et al., 2007) can explain the decrease in TFC measured on August 25th harvest. Other research also reported that the variation of TFC is linked with the weather conditions, showing significant changes from one year to the other (Tolić et al., 2017). In Figure 2, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro -Wilk test $P=0.7536$, Levene's test $P=0.471$, one-way ANOVA $P<0.001$).

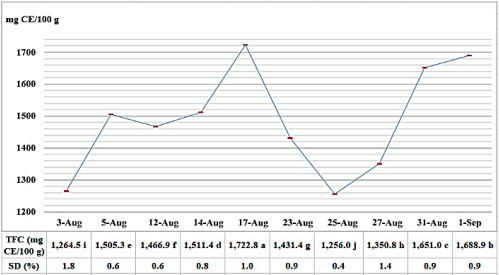


Figure 2. Variation of TFC (mg CE/100 g) in *Aronia melanocarpa* fruit samples during harvest

Total anthocyanins (TA)

Anthocyanins are antioxidants with several health benefits, including anticancer, antiatherogenic, and anti-inflammatory properties, which have been extensively studied for their health advantages over the last two decades. Anthocyanins in foods are key quality indicators that influence customer preferences, and their stability in food is altered by various factors, including pH, solvents, temperature, oxygen, enzymes, and other compounds (Teneva et al., 2022). TA had the highest value at the end of August, 45.91% more than at the start of the harvest

(Figure 3). Anthocyanin synthesis is initiated and regulated by the plant hormone abscisic acid (ABA) and variation is influenced by different external factors like light exposure, temperature, nutritional factors (Zoratti et al., 2014).

There are different factors that determine anthocyanin degradation: chemical degradation due to increase of pH in the vacuole microenvironment, external temperature and light exposure; enzymatic degradation by polyphenol oxidase (PPO) and peroxidase (Zhao et al., 2021), explaining the lowest concentrations in August 27th and September 1st harvests.

Engin & Mert (2020) reported values between 558.3 mg CGE/100 g and 843.9 mg CGE/100 g and that anthocyanin content in aronia berries in Turkey increased during ripening; however, it decreased due to overripening.

In Figure 3, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.5019$, Levene's test $P=0.549$, one-way ANOVA $P<0.001$).

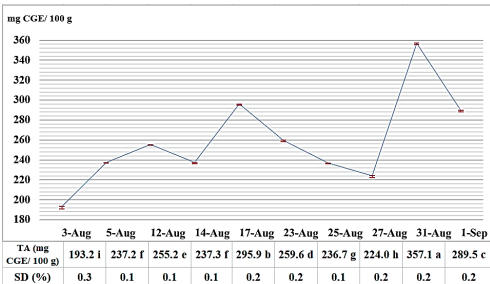


Figure 3. Variation of TAC (mg CGE/100 g) in *Aronia melanocarpa* fruit samples during harvest

Total antioxidant capacity (TAC)

In purple colour fruits, the main responsible compounds for a high TAC are anthocyanins (Valero and Serrano, 2013). During harvest, TAC variation (Figure 4) had a similar pattern as the variation of TA (Figure 3), the highest TAC being recorded on August 31st. Degradation of anthocyanins can determine the decrease of TAC, explaining the low values recorded on August 27th and September 1st.

Other studies show a similar pattern; Engin & Mert (2020) reported an 8% increase for an aronia cultivar in Turkey in the first four harvest dates and a gradual decrease between dates four and six of harvest. Bolling et al. (2015) reported a decrease of the antioxidant capacity

in the first half of august for an aronia cultivar in USA, followed by a steady increase until mid-September.

In Figure 4, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.7617$, Levene's test for equality of error variances $P=0.341$, one-way ANOVA $P<0.001$).

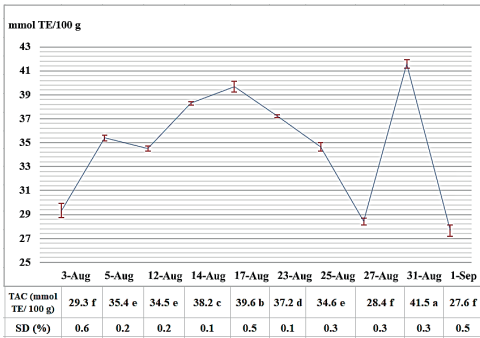


Figure 4. Variation of TAC (mmol TE/100 g) in *Aronia melanocarpa* fruit samples during harvest

The ferric reducing antioxidant power (FRAP)

FRAP was used to measure antioxidant activity of fruits during ripening. The reducing power is primarily associated with the presence of reducing agents, which exhibit antioxidant activity by interrupting free radical chain reactions through the donation of a hydrogen atom (Tolić et al., 2015). Higher total phenolic content (TPC) often correlates with increased FRAP values (Subbiah et al., 2020). FRAP varies from one harvest to the other (Figure 5), with a low peak at the beginning of September and the highest value on 27-Aug harvest. Other studies reported values between 13.50 mmol Fe(II) equivalent/100 g to 68.60 mmol Fe(II) equivalent/100 g (Tolić et al., 2015).

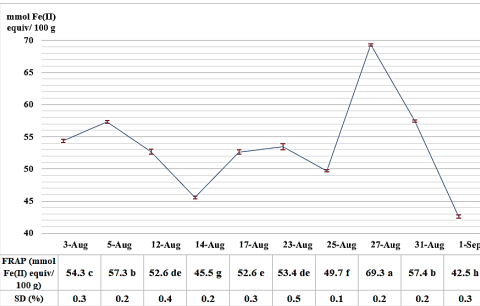


Figure 5. Variation of FRAP (mmol Fe(II) equiv/100 g) in *Aronia melanocarpa* fruit samples during harvest

In Figure 5, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.7155$, Levene's test $P=0.238$, one-way ANOVA $P<0.001$).

Mineral concentrations

The total mineral concentrations during harvest are presented in Figures 6 to 19.

Dietary macro nutrients

Calcium (Ca) accumulation in fruits is highly dependent on water delivery. Also, Ca concentration in fruits depends on plant species, on cell wall interactions in the apoplast (Hocking et al., 2016). The highest concentrations of Ca have been recorded on August 5th and August 27th (Figure 6). Other authors reported values of 119 mg/kg and 552 mg/kg (Šnebergrová et al., 2014), 601 mg/kg and 1167 mg/kg (Pavlovic et al., 2015), 1,212 mg/kg (Cindrić et al., 2017) and 3,220 mg/kg (Lancrajan, 2012). These large differences in values might be due to the different harvest dates, rainfall regime and varieties/cultivars of Aronia. According to the Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, the daily recommended doze for adults is 1,000 mg Ca/day (Norm 13/12/2000 - Romanian Legislative Portal, 2025). In Figure 6, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.7105$, Levene's test $P=0.384$, one-way ANOVA $P<0.001$).

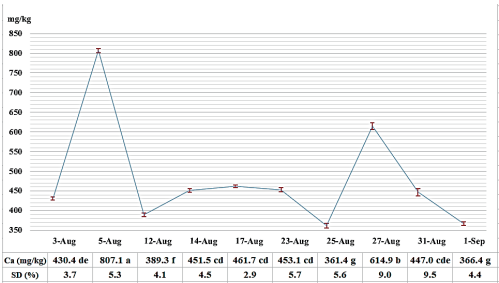


Figure 6. Variation of Ca concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Potassium (K) is an essential nutrient that influences the majority of biochemical and physiological processes involved in plant development and metabolism. It also helps plants survive a variety of biotic and abiotic stressors (Wang et al., 2013). However low-K

fruits for patients with chronic kidney disease are of major importance (Cui et al., 2024). During harvest, K in aronia berries had the highest concentrations in the first half of August and the lowest concentration was found on 17 august (Figure 7). Other studies have shown concentrations between 2,707-4,977 mg/kg (Pavlovic et al., 2015), 6,790 mg/kg (Cindrić et al., 2017), and 2,180 mg/kg (Lancrajan, 2012).

According to the Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, the recommended daily dose of K for healthy adults is 3.50 g/day (Norm 13/12/2000 - Romanian Legislative Portal, 2025).

In Figure 7, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.9779$, Levene's test for equality of error variances $P=0.096$, one-way ANOVA $P<0.001$).

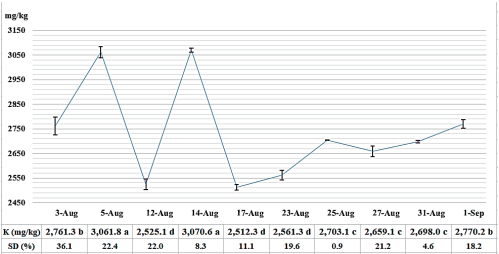


Figure 7. Variation of K concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Magnesium (Mg) is well known for its various effects on the human body and is important for nerve transmission and neuromuscular conduction (Kirkland et al., 2018). According to the Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, the recommended daily doze for healthy adults is 350 mg Mg /day (Norm 13/12/2000 - Romanian Legislative Portal, 2025).

During harvest, Mg in aronia berries shows a high peak at the beginning of the harvest (Figure 8) and it gradually decreases until the end of harvest. Other studies have shown concentrations between 164-578 mg/kg (Pavlovic et al., 2015), 669 mg/kg (Cindrić et al., 2017), and 168 mg/kg (Lancrajan, 2012). In Figure 8, (Shapiro-Wilk test $P=0.9269$, Levene's test $P=0.045$, one-way ANOVA

P<0.001) data followed by the same letter are not significantly different for $\alpha=0.05$.

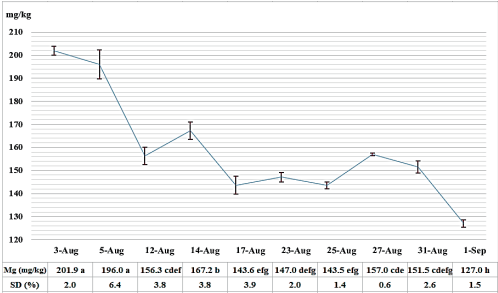


Figure 8. Variation of Mg concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Both World Health Organization (*Salt Intake*, 2024) and Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, recommend an intake of maximum 2 g of sodium (Na) per day (Norm 13/12/2000 - Romanian Legislative Portal, 2025). During harvest, Na in aronia berries shows a fluctuation in values, with the lowest amount being recorded on August 27th harvest, and the highest on August 3rd (Figure 9). Other studies have shown concentrations of Na between 12.5-16.8 mg/kg (Pavlovic et al., 2015), 4.27 mg/kg (Cindric et al., 2017) and 26 mg/kg (Lancrajan, 2012).

In Figure 9, data followed by the same letter are not significantly different for $\alpha= 0.05$ (Shapiro-Wilk test $P=0.522$, Levene's test $P=0.004$, one-way ANOVA $P<0.001$).

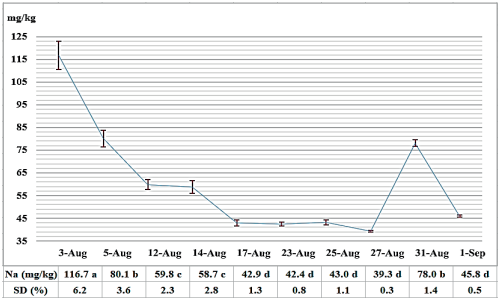


Figure 9. Variation of Na concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Dietary micro nutrients

Chromium (Cr), an important mineral, appears to play a favorable role in the control of insulin activity and its effects on glucose, protein, and

lipid metabolism (Havel, 2004). In the presence of Cr in its physiologically active form, significantly lower quantities of insulin are required in the human body (Anderson, 2003). The National Institute of Health in USA recommends the daily intake of Cr of 25 micrograms/day for adult females and 35 micrograms/day for adult males (*Dietary Reference Intakes (DRIs): Recommended Dietary Allowances and Adequate Intakes, Elements, Food and Nutrition Board, National Academies*, 2025). Cr in fruits can vary due to soil condition and sampling location, depending on the location where the fruits are growing on the plant; also pH of soil and humidity will influence the Cr uptake by plants (Banks et al., 2006). During harvest, the lowest amount of Cr was recorded on August 25th harvest, and the highest on August 23rd (Figure 10). Other studies have shown concentrations between 0.49-0.53 mg/kg (Pavlovic et al., 2015) and 0.029 mg/kg (Cindric et al., 2017).

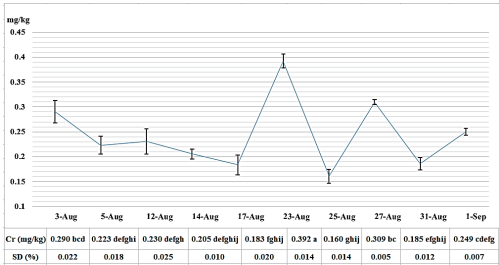


Figure 10. Variation of Cr concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest.

In Figure 10, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.8437$, Levene's test $P=0.380$, one-way ANOVA $P<0.001$).

Copper (Cu) is an essential mineral that occurs naturally in some foods; it is accessible as a dietary supplement and is a cofactor for various enzymes (known as cuproenzymes) in energy production, iron metabolism, neuropeptide activation, connective tissue formation, and neurotransmitter synthesis (Ross et al., 2012). After iron, Cu has gathered a lot of interest in cell death, particularly in causing tumor cell death, inducing autophagy or apoptosis in tumor cells via a variety of mechanisms of action (activation of stress pathways, cell cycle arrest, inhibition of angiogenesis, cuproptosis,

and paraptosis), all of which are promising in cancer therapy and have emerged as new hotspots in research (Ji et al., 2023). According to the Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, the recommended daily doze for adults is 3 mg Cu/day (Norm 13/12/2000 - Romanian Legislative Portal, 2025).

During harvest, Cu in aronia berries shows a concentration fluctuation, with the lowest level being recorded on August 3rd and 5th harvests, and the highest on August 23rd (Figure 11). Other studies have shown concentrations between 0.82-2.11 mg/kg (Djuric et al., 2015; Pavlovic et al., 2015).

In Figure 11, data followed by the same letter are not significantly different for $\alpha=0.05$. (Shapiro-Wilk test $P=0.9805$, Levene's test $P=0.119$, one-way ANOVA $P<0.001$).

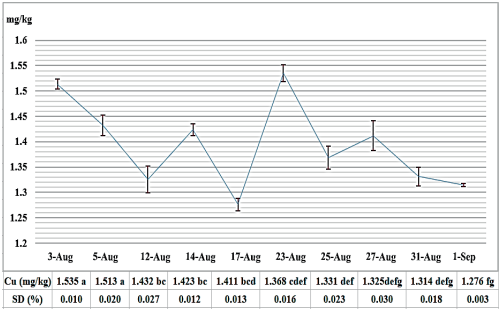


Figure 11. Variation of Cu concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Iron (Fe) is a mineral found naturally in many foods and is accessible as a nutritional supplement. Fe is an important component of hemoglobin, an erythrocyte (red blood cell) protein that transports oxygen from the lungs to tissues (Ross et al., 2012). According to the Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, the recommended daily doze for adults is 18 mg Fe /day (Norm 13/12/2000 - Romanian Legislative Portal, 2025).

During harvest, Fe in aronia berries shows a great and inconsistent fluctuation in values, ranging from 5.56 mg/kg on August 17th harvest to 110.69 mg/kg on August 23rd harvest (Figure 12). Other studies have shown concentrations between 9.4-14.2 mg/kg (Pavlovic et al., 2015), 1.32 mg/kg (Cindrić et al., 2017) and 9.3 mg/kg (Lancrajan, 2012).

In Figure 12, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.0242$ - reject normality), Levene's test for equality of error variances $P<0.001$, Kruskal-Wallis test $P=0.000753$).

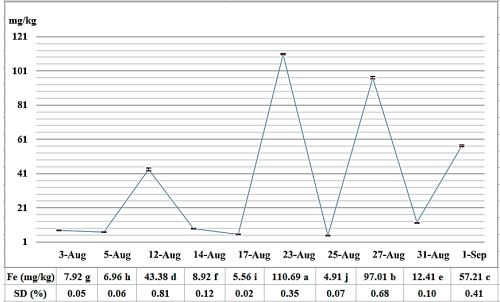


Figure 12. Variation of Fe concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Manganese (Mn) is a necessary trace element that can be obtained as a dietary supplement or found naturally in a variety of foods (Ross et al., 2012). Mn is necessary for healthy cellular homeostasis, growth, and development. High Mn exposure results in clinical illness with extrapyramidal symptoms that mimic idiopathic Parkinson's disease (Bowman et al., 2011). There is no evidence in research to support health risks associated with excessive manganese consumption (Finley et al., 2003).

According to the Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, the recommended daily doze for adults is 3 mg Mn /day (Norm 13/12/2000 - Romanian Legislative Portal, 2025). According to the USA National Institute of Health – Office of Dietary Supplements, the adequate intake of Mn is 2.3 mg for adult males and 1.8 mg for adult females (*Dietary Reference Intakes (DRIs): Recommended Dietary Allowances and Adequate Intakes, Elements, Food and Nutrition Board, National Academies*, 2025).

During harvest, Mn in aronia berries shows a fluctuation in values, with the lowest amount being recorded on August 12 harvest, 3.48 mg/kg the highest on August 27th, 9.20 mg/kg (Figure 13). Other studies reported concentrations between 5.49-17.89 mg/kg (Pavlovic et al., 2015) and 0.82 mg/kg (Cindrić et al., 2017).

In Figure 13, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.9805$, Levene's test for equality of error variances $P=0.036$, one-way ANOVA $P<0.001$).

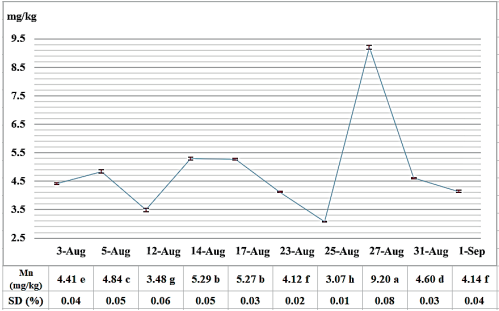


Figure 13. Variation of Mn concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Zinc (Zn) in aronia berries exhibits minimal fluctuations in values during August, with the lowest amount reported on August 17th, and a surge in concentration on August 31st (Figure 14). Other studies report values ranging from 4.09-8.40 mg/kg (Pavlovic et al., 2015) and 0.55 mg/kg (Cindrić et al., 2017). According to the Romanian Norm from December 13, 2000, emitted by the Romanian Ministry of Health, the recommended daily doze for adults is 15 mg Zn /day (Norm 13/12/2000 - Romanian Legislative Portal, 2025). According to the USA Office of Dietary Supplements, the adequate intake of Zn is 8 mg for adult males and 11 mg for adult females (*Dietary Reference Intakes (DRIs): Recommended Dietary Allowances and Adequate Intakes, Elements, Food and Nutrition Board, National Academies*, 2025).

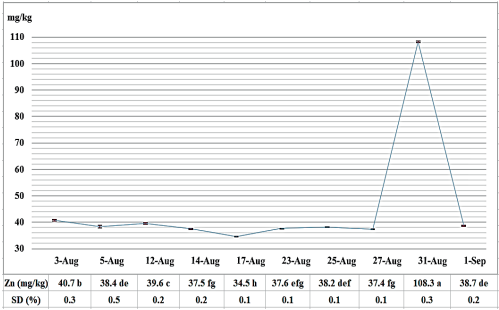


Figure 14. Variation of Zn concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

In Figure 14, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.6960$, Levene's test for equality of error variances $P=0.060$, one-way ANOVA $P<0.001$).

Dietary ultra trace elements

Aluminium (Al) concentrations show a great variation throughout harvest, as shown in Figure 15, the lower value being 2.85 mg/kg and the highest 7.41 mg/kg. Other research have shown between 2.88-4.40 mg/kg (Pavlovic et al., 2015), or 158 mg/kg (Cindrić et al., 2017). According to the European Food Safety Authority (EFSA), a tolerable intake of 1 mg Al/kg body weight/week is acceptable (Authority, E. F. S. 2008). Al can be found in fruits either due to intake from the geologic environment throughout growth, or from any potential contamination from Al articles that come into touch with food and additives, as well as veterinary medications, fertilizers, and the air (Stahl et al., 2011).

In Figure 15, data followed by the same letter are not significantly different for $\alpha= 0.05$ (Shapiro-Wilk test $P=0.2729$, Levene's test for equality of error variances $P=0.002$, one-way ANOVA $P<0.001$).

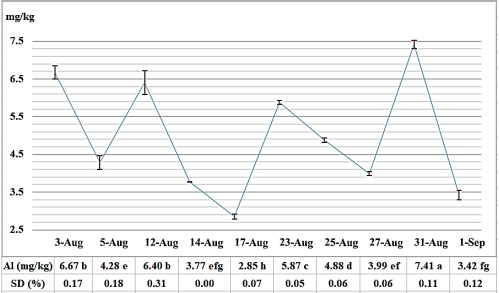


Figure 15. Variation of Al concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

During harvest, boron (B) in aronia berries showed a gradual decrease from 190 mg/kg at the beginning of August to 119.69 mg/kg at the end of August (Figure 16). Other studies show concentrations around ten times lower, 2.88-14.22 mg/kg (Pavlovic et al., 2015). B is a trace element found naturally in many foods and drinking water (Kuru et al., 2019). It is a structural component of plant cell walls and is necessary for plant growth, pollination, and

seed production (Nielsen and Eckhart, 2020). Some clinical investigations in humans suggest that B may be useful for lowering the symptoms of osteoarthritis, probably by preventing inflammation (Miljkovic et al., 2009). B is a critical nutrient for plant growth, development, production, and quality. It serves numerous important functions in plants, including cell wall synthesis and structural integration. During pollen tube growth and germination, B increases the likelihood of fruit setting and seed production, resulting in higher crop productivity (Shireen et al., 2018). In Figure 16, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.0544$, Levene's test for equality of error variances $P=0.012$, one-way ANOVA $P<0.001$).

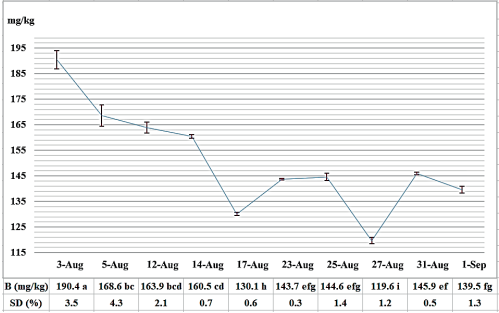


Figure 16. Variation of B concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Barium (Ba) in aronia berries showed a fluctuation in values during harvest, with the lowest amount being recorded on August 12 harvest, 2.01 mg/kg the highest on August 27th, 4.46 mg/kg (Figure 17). Other studies show concentrations between 1.48-6.66 mg/kg (Pavlovic et al., 2015). The European Commission for Public Health and Risk Assessment determined a tolerable daily intake of 0.02 mg Ba/kg bw/day (SCHER, 2012). Eating or drinking significant amounts of Ba compounds that dissolve in water or the stomach can cause comprising kidney diseases, neurological, cardiovascular, mental, and metabolic disorders (Peana et al., 2021). In Figure 17, data followed by the same letter are not significantly different for $\alpha= 0.05$ (Shapiro-Wilk test $P=0.0205$ (reject normality),

Levene's test for equality of error variances $P=0.002$, Kruskal-Wallis test $P=0.000753$).

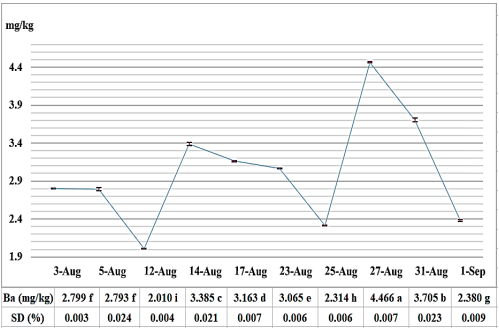


Figure 17. Variation of Ba concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Nickel (Ni) is a transitional element that is widely diffused in the environment, including air, water, and soil. This could be the result of both natural and human action (Genchi et al., 2020). Ni has been shown to disrupt the photosynthetic activity of higher plants; it can significantly degrade soil fertility and induce chronic diseases in humans (Begum et al., 2022). Even though Ni is a beneficial element for human health, helping microorganisms colonize the gut, exposure to it also represents a potential danger for the human body, such as allergies, nickel-induced carcinogenesis, or infectious disease based on bacteria that rely on nickel-based enzymes to colonize the host (Zambelli and Ciurli, 2013). According to EFSA, the tolerable daily intake of Ni should not exceed 13 $\mu\text{g/kg}$ body weight, around 0.78 mg/day for the average 60 kg adult (Dieter et al., 2020). During harvest, Ni in aronia berries shows a fluctuation in values, with the lowest amount being recorded on August 12 harvest, and the highest on August 27 (Figure 18). Other studies have shown concentrations between 0.143-0.741 mg/kg (Pavlovic et al., 2015) and 0.38 mg/kg (Cindrić et al., 2017). In Figure 18, data followed by the same letter are not significantly different for $\alpha=0.05$ (Shapiro-Wilk test $P=0.2299$, Levene's test for equality of error variances $P=0.160$, one-way ANOVA $P<0.001$).

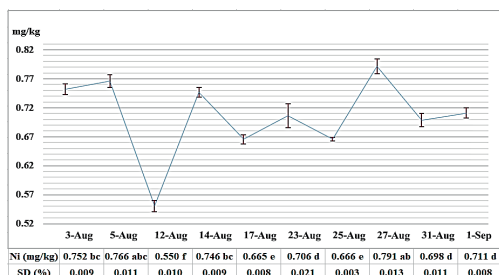


Figure 18. Variation of Ni concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

Strontium (Sr) is a common element in the environment, found in all living organisms (Höllriegel 2019). Sr is very important for human health, participating in various physiological functions and biochemical effects, having a protective effect on bone diseases, dental caries, and cardiovascular diseases, but also maintaining reproductive health and having great prospects in the development of health products and natural medicines (Huang et al., 2023). During harvest, Sr in aronia berries shows a fluctuation in values, with the lowest amount being recorded on August 12th harvest, and the highest on August 3rd (Figure 19).

In Figure 19, data followed by the same letter are not significantly different for $\alpha=0.05$, (Shapiro-Wilk test $P=0.9805$, Levene's test $P=0.014$, one-way ANOVA $P<0.001$).

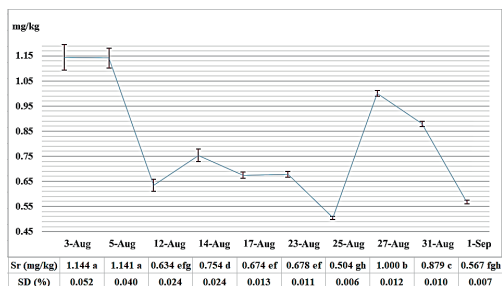


Figure 19. Variation of Sr concentrations (mg/kg) in *Aronia melanocarpa* fruit samples during harvest

CONCLUSIONS

Aronia melanocarpa fruits may be used in the development of personalised foods as an important source of polyphenols and macro and micro minerals.

Due to the high content of polyphenols, spike of anthocyanins, and decrease of flavonoids, the optimum harvest dates were determined to be August 17th and August 31st.

The spike in K on August 5th and August 14th harvests correlated with the decrease in Ca after August 14th can be associated with the ripening of the berries.

The most valuable harvests from the mineral point of view were the August 23rd harvest for high amounts of Cu, Fe, and Cr, August 31st for zinc, and August 27th for Mn.

The harvest with the maximum mineral concentrations was during the first two weeks of August, and the one with the maximum polyphenol concentrations was in the last weeks of August and beginning of September. Overall, the findings of this study demonstrated that the time of harvest will be important for the use of aronia berry in the development of antioxidant-rich and mineral-rich solid and liquid personalised food products.

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