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The Effect of Soil Contamination on Chemical Composition and Quality of Aronia (*Aronia melanocarpa*) Fruits

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***Abstract*—**A field study was conducted to evaluate the chemical composition and quality of the Aronia fruits, as well as the possibilities of Aronia cultivation on soils contaminated with heavy metals. The experiment was performed on an agricultural field contaminated by the Non-Ferrous-Metal Works (NFMW) near Plovdiv, Bulgaria. The study included four varieties of Aronia; Aron variety, Hugin variety, Viking variety and Nero variety. The Aronia was cultivated according to the conventional technology on areas at a different distance from the source of pollution NFMW- Plovdiv (1 km, 3.5 km, and 15 km). The concentrations of macroelements, microelements, and heavy metals in Aronia fruits were determined. The dry matter content, ash, sugars, proteins, and fats were also determined. Aronia is a crop that is tolerant to heavy metals and can successfully be grown on soils contaminated with heavy metals. The increased content of heavy metals in the soil leads to less absorption of the nutrients (Ca, Mg and P) in the fruit of the Aronia. Soil pollution with heavy metals does not affect the quality of the Aronia fruit varieties.

***Keywords*—**Aronia, chemical composition, fruits, quality.

I. Introduction

ARONIA (*Aronia melanocarpa*) belongs to the Aronia subgenus of the Rosaceae family. It is also known by its Russian name "chernaya ryabina" ("black chokeberry"). The following varieties of aronia are grown in Europe: Aron variety (Denmark), Nero variety (Czech Republic), Viking variety (Finland), Rubin variety (Russia through Finland), Kurkumäcki variety (Finland), Hugin variety (Sweden), Fertödi variety (Hungary), Galicjanka variety (Poland) [1], as the most popular are 6 species of Aronia varieties - Nero variety, Galicanka variety, Viking variety, Fert variety, Hugin variety and Aron variety. They differ from each other by efficiency of juice extraction, fruit composition (content of total polyphenols, anthocyanins and proanthocyanidins, total antioxidant capacity) as well as weight and fruit diameter [2], [3]. Due to the high content of anthocyanins and purple pigment in fruits, aronia is used as a natural colouring agent in food and pharmaceutical industry. Aronia is mainly used for the production of aronia juices and syrups. Fruits can also be eaten raw, dried or can be used to prepare compotes, jams, wines and liqueurs. Thanks to the sour and tangy flavour of aronia, juice consumers prefer to consume juices in combination with other types of fruits such as apple, pear and blackcurrant [4].

The chemical composition of aronia varies and depends on many factors, and above all on the genotype (or hybrid), degree of maturity, climate, harvest date and fertilizer use [5], [6]. Phenolic compounds are the most important ingredients present in aronia, which directly affect the healing properties. Fruits have a high content of procyanidins, anthocyanins and phenolic acids. Procyanidins, oligomeric and polymer (epi) catechins (1578-8191 mg/100 g dry weight) are defined as the basic class of polyphenol compounds in aronia [7].

The content of heavy metals in aronia fruits may vary depending on the place of harvest and the vegetation period [8]. Consuming foods containing heavy metals over a short period of time can cause problems with the digestive system such as constipation, vomiting, weight loss, abdominal pain, behavioural change, anemia, lethargy, as well as high blood pressure, nervous disorders, problems with memory and concentration.

Recent studies have shown that the use of fertilizers can have a different impact on the chemical composition of aronia fruis, especially with respect to the sugar content and the quantity and profile of phenols [6]. The effect of microelements on the accumulation of anthocyanins in the fruits of *Aronia melanocarpa* has also been studied [9].

In the scientific literature the data on the mineral content of the fruits are very scarce. There are only a few studies of the mineral content of this fruit [10]-[12]. Therefore, it is important to determine the nutritional composition, as well as the levels of potentially toxic elements in aronia fruits.

The aim of the present study is to conduct a comparative study that will allow us to determine the quantities and deposits of the accumulation of macro, microelements and heavy metals in the vegetative organs of four varieties of aronia (Aron variety, Hugin variety, Viking variety, Nero variety), the composition and quality of the fruits, as well as to determine the possibilities for its cultivation on heavy metal contaminated soils.

II. Material and Methods

The survey was conducted in the period 2014-2016. The study included four varieties of aronia (Aron variety, Hugin variety, Viking variety and Nero variety). Aronia was cultivated according to the conventional technology on areas at a different distance from the source of pollution KCM -

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Plovdiv/non-ferrous metal plant/ (1 km, 3.5 km and 15 km).

In the technological maturity phase samples of plant material (stems, leaves and fruits) from aronia were taken for analysis. Fruits were analyzed in a fresh state for the content of macro, microelements and heavy metals were determined by the method of the microwave mineralization. To determine the chemical composition in the samples, inductively coupled emission spectrometry (Jobin Yvon Emission -JY 38 S, France) was used. The organic composition of fruits was also determined. The content of dry matter, ash, sugars, proteins and fats was determined according to the standardized methods [13], [14].

III. Results and Discussion

To clarify the degree of soil contamination with heavy metals and their localization in the vegetative organisms of aronia, soil samples were taken from areas at different distances from KCM - Plovdiv (0.1, 3.5 and 15 km). The physical and chemical properties of soil samples are presented in Table I. Soils are characterized by a slightly alkaline reaction, an average organic carbon content and a medium to high nutrient content (N, P, K) (Table I).

The results presented in Table I show that with moving away from KCM - Plovdiv, there is a well-known tendency to reduce the total content of heavy metals in the soil. In soil samples taken from the 1 km distance area, Pb values were reported exceeding the maximum permissible concentrations/ MPC/(60 mg/kg) (515.7 mg/kg). In samples taken from point 2 (3.5 km from KCM) and point 3 (15 km from KCM), the Pb values decreased to 83.1 mg/kg and 24.6 mg/kg, respectively. Similar results are obtained for Cd and Zn. The reported values for the soils from point 1 are significantly above the MPC. At point 1 (1 km from KCM), 1078 mg/kg Zn and 11.5 mg/kg Cd were reported, at point 2, 215.3 mg/kg Zn and 4 mg/kg Cd were reported, and in the area located 15 km from KCM (point 3) 33.9 mg/kg Zn and 2.7 mg/kg Cd were found. The content of Cu in the soils from the survey areas is significantly lower than the threshold limit concentration/TLC /accepted for Bulgaria - 60 mg/kg.

The results for the mobile forms of metals determined with DTPA indicate that the Pb and Cd mobile forms in contaminated soils account for most of its total content, followed by Zn and Cu. In terms of Cd, they range from 56.2% (1 km) to 45.4% (3.5 km). Similar results were obtained with Pb and Zn. The mobile forms of Pb range from 64.8 (1 km) to 25% (3.5 km), Zn from 27% (1 km) to 8.7% (3.5 km), and Cu - from 41.2% (1 km) to 19.3% (3.5 km).

In uncontaminated soils, again the Cd mobile forms are the largest part of its total content, reaching up to 24.8%, followed by Cu and Zn with 10% and Pb with 8.5%.

The content of macro, microelements and heavy metals in aronia fruits is presented in Fig. 1. The results obtained show that the macroelements (K, P, Mg, Ca) predominate in aronia fruits, followed by Zn and Fe. The content of Cu and Mn is significantly lower. Aronia fruits contain the toxic metals Pb and Cd. The accumulation of heavy metals in the fruits is possible on the conductive system and depends primarily on the variety and the element under consideration.

TABLE I
Characterization of the Soils

Parameter	Soil 1 1 km	Soil 2 3.5 km	Soil 3 15 km
pH	7.3	7.6	7.5
EC, dS/m	0.20	0.15	0.15
Organic content, %	2.39	2.24	1.54
N Kjeldal, %	0.17	0.22	0.13
Pb, mg/kg	515.7	83.1	24.6
Cd, mg/kg	11.5	4	2.7
Zn, mg/kg	1078	215.3	33.9
Cu, mg/kg	101.9	71.3	16.0
Fe, mg/kg	14865	29581.9	27113.4
Mn, mg/kg	461.3	884.2	884.2
K, mg/kg	3381.5	6780	6780.0
Ca, mg/kg	90200	18065	16060.6
Mg, mg/kg	9035	10040.1	10040.0
P, mg/kg	473.6	387.3	354.9

TLC (pH 6.0-7.4) – Pb -60 mg/kg, Cd-2.0 mg.kg, Zn-320 mg/kg. TLC (pH >7.4) – Pb – 100 mg/kg, Cd – 3.0 mg/kg, Zn -400 mg/kg

TABLE II
DTPA- Extractable Pb, Zn, Cd and Cu in Soils Sampled from KCM

Soils	Pb		Zn		Cd		Cu	
	mg/kg	%*	mg/kg	%*	mg/kg	%*	mg/kg	%*
S1	289.6	56.2	291.4	27.0	7.4	64.8	42.0	41.2
S2	37.9	45.4	18.7	8.7	0.75	25.0	13.8	19.3
S3	2.1	8.5	2.4	7.1	0.67	24.8	1.6	10.0

*DTPA extractable/total content

By moving away from the source of contamination there is a pronounced tendency for reduction of the heavy metal content in the fruits of Aron variety (Fig. 1). The Pb content in aronia fruit grown at 1 km (point 1) reaches up to 0.2 mg/kg, Zn - to 4.7 mg/kg and Cd - to 0.05 mg/kg. The Pb content in aronia fruits from point 2 (3.5 km from KCM) decreases to 0.1 mg/kg, Zn to 3.9 mg/kg and Cd to 0.02 mg/kg. In aronia grown in the area located 15 km from KCM, the reported values are significantly lower - 0.02 mg/kg Pb, 4.3 mg/kg Zn, and the Cd content is below the limits of the quantitative measurement of the method used. Similar results are obtained from [8], who study aronia fruits collected from unpolluted and polluted sites in Poland. In terms of Cd content, there was no effect of contamination, whereas with Pb four times higher concentration was found in fruits grown on contaminated soil.

The content of Cd and Pb in the fruits of Aron variety, grown 1 km from KCM, is within the maximum permissible limits. According to the European standards, the Cd and Pb content of the fruits must not exceed the values of 0.05 mg/kg fresh weight for Cd and 0.2 mg/kg fresh weight for Pb [15].

The results we obtained are consistent with that found by [8] and [16] that the accumulation of toxic metals, pesticides, nitrates(III) and nitrates(V) in aronia fruits is very low. According to the authors, the content of heavy metals (Pb, Cd) in aronia fruits can change depending on the place of harvest and the vegetation period of development.

There is almost no evidence in the literature on the contamination of aronia fruits. According to the literature [12],

the content of Pb and Cd in aronia fruits is in the range of not detectable (n.d)-0.205 mg/kg, and 0.016-0.064 mg/kg, respectively. The content of toxic metals in most foods is regulated by EC [15].

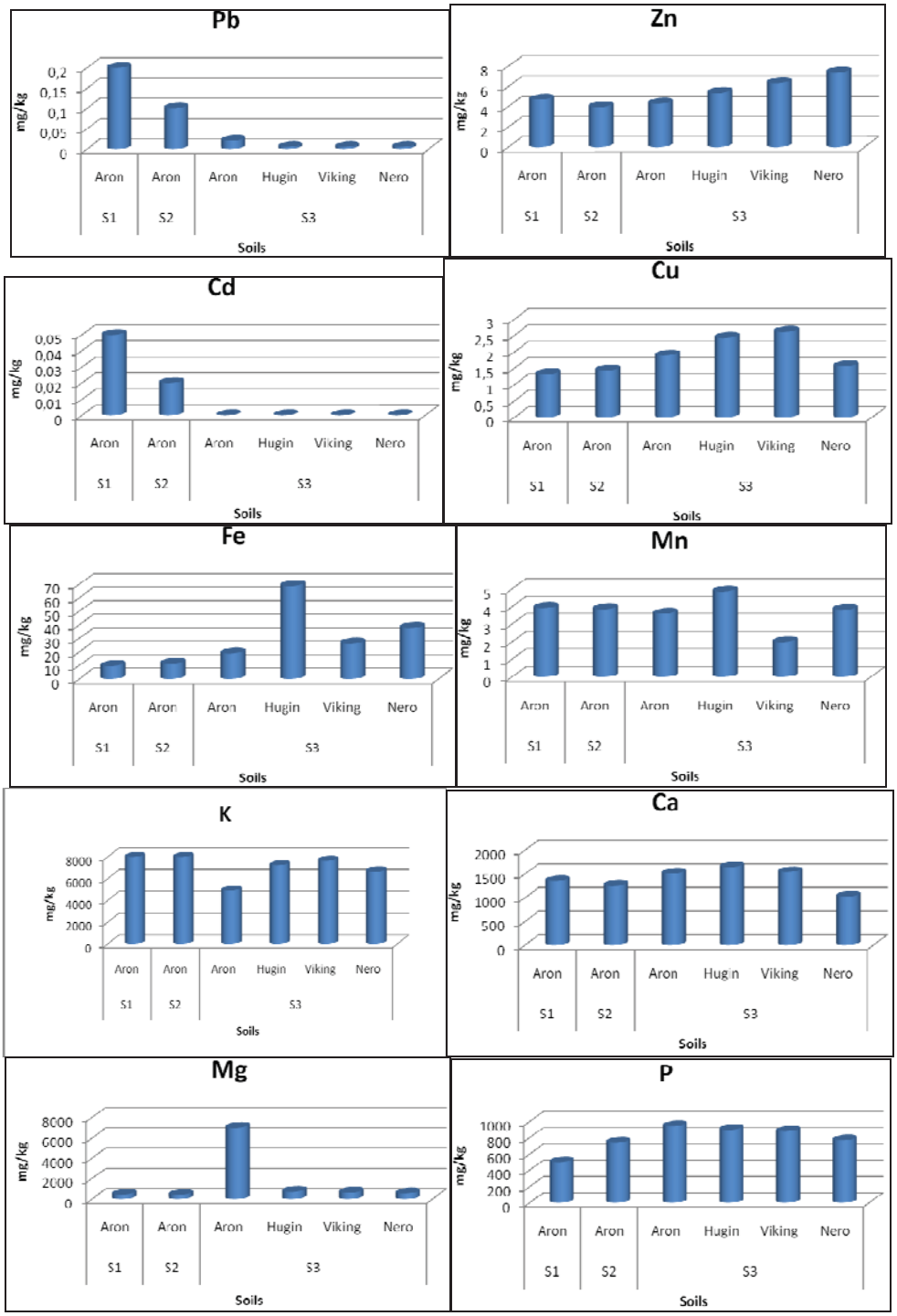

Fig. 1 Content of heavy metals, micro and macroelements (mg/kg) in fruits of Aronia

The measured Pb and Cd concentrations for the different aronia varieties grown at 15 km from KCM are below the maximum permissible limits for Pb and Cd in food (0.20 mg/kg and 0.05 mg/kg, respectively).

With respect to Cu and Fe, the opposite tendency is observed and their amount in the aronia fruit increases. The Cu content increases from 1.3 (point 1) to 1.9 mg/kg (point 3) and from 9.5 mg/kg (point 1) to 18.8 (point 3) with Fe.

By removing the source of contamination there is a pronounced tendency to increase the content of micro and macroelements in fruits of Aron variety (Fig. 1). The K, Ca, Mg and P content is increased, respectively, with K from

5330.0 mg/kg (point 1) to 7916.5 mg/kg (point 3), with Ca - from 1407.7 to 1588.5 mg/kg, with Mg - from 431,3 mg/kg (point 1) to 698.2 mg/kg (point 3) and with P - from 500.8 mg/kg to 940 mg/kg.

Variety peculiarities are observed in the accumulation of the elements of the aronia fruits when grown on unpolluted soil (point 3). The resulting differences on the accumulation of the elements in the fruits are due to the influence of soil composition, maturity state, climate and environment and genetic background, these differences are expected [17].

The highest values in aronia fruits grown at 15 km from KCM (point 3) were found for Pb, Mg and P in Aron variety, Zn in Nero variety, Cu in Viking variety, Fe, Mn, K and Ca in Hugin variety (Fig. 1). The content of Pb in aronia fruit ranges from 0.03 mg/kg in Nero variety to 0.02 mg/kg in Aron variety, Zn from 4.3 mg/kg in Aron variety to 7.4 mg/kg in Nero variety, Cd is below the limits of the quantitative measurement of the method used, Cu - from 1.5 mg/kg in Nero variety to 2.6 mg/kg in Viking variety, Fe - from 18.8 mg/kg in Aron variety to 68.6 mg/kg in Hugin variety, Mn-from 20.3 mg/kg in Viking variety to 48.6 mg/kg in Viking variety, K from 6328.1 mg/kg in Nero variety to 7995.0 mg/kg in Hugin variety, Ca - from 1026.2 in Nero variety to 1648.7 mg/kg in Hugin variety, Mg-from 538.1 mg/kg in Nero variety to 698.2 mg/kg in Aron variety and P - from 765.4 mg/kg in Nero variety to 940.8 mg/kg in Aron variety.

The results we obtained are consistent with the results of [12], who established the following values for the elemental composition of aronia fruits - K (3.842 mg/kg), Ca (884 mg/kg), P (598 mg/kg), Mg (371 mg/kg), 11.8 mg/kg, Mn (11.7 mg/kg), Zn (6.25 mg/kg), Cu (1.47 mg/kg). Similar results were also found by [18] for Fe, Cu and Zn in fruits (12.15 mg/kg Fe, 1.65 mg/kg Cu and 8.09 mg/kg Zn).

According to [19], metal absorption and accumulation in plants cause a reduction in K, Ca and Mg in plants, especially in the above-ground parts, indicating that heavy metals affect not only the absorption of nutrients, but also the distribution of nutrients in different parts of the plant. This is also confirmed by the results obtained for aronia fruits in the cultivation of aronia on contaminated soil (point 1).

The organic composition of aronia fruits is affected by factors such as variety, fertilization, fruit maturation, harvest date or habitat/location [6].

Fig. 2 shows data of titrated acidity, content of dry matter, sugars, proteins, fats and ash in aronia fruits.

Dry matter content of aronia fruits ranges from 56.4% for Viking variety to 86.2% for Aron variety, which does not correspond to the results obtained by [6]. According to the authors, the dry matter content in fruits ranges from 17% to 30%.

It is known that aronia is high in dietary fiber - cellulose, hemicellulose and lignin [20], which can act as weak sorbents of cadmium [21]. Aronia fruit has been found to contain dietary fibre at 5.62 g/100 g (fresh weight) [17]. Fresh fruits have a relatively low pectin content (0.3-0.6%) [22], [23]. Through the NMR analysis, the following compounds contained in the dietary fiber were identified: microcrystalline cellulose, pectins, lignins, polymeric copolymers and condensed tannins.

The titratable acidity values range from 1.34% to 3.07% for the different varieties of aronia (Fig. 2). The tested fruits are characterized by a low content of organic acids. The lowest is the content of acid in Aron variety (1.34-1.86). Their content is significantly higher in Hugin variety (3.07). According to [17], [22], [24], the total organic acid content is relatively low in aronia fruits (1-1.5%) compared to other fruits. The main acids identified in the fruits are L-malic acid and citric acid [17], [22].

The results we obtained show that the amount of sugars in aronia fruits ranges from 27.7% for Aron variety to 36.6% for Viking variety (Fig. 2). The total sugar content obtained by [16] reaches 6.2-10.8 g in 100 grams of fresh fruit. The results obtained by [25] show that the level of reducing sugars in the analyzed fruits ranges from 8.83 g ("Viking") to 12.48 g ("Hugin"). According to the literature, the content of reducing sugars in fresh fruits is between 16 and 18% [23]. According to other authors [26], [27], the sum of glucose and fructose is estimated to be between 13-17.6 g/100 g of fresh weight, with no sucrose detected.

The highest is the fat content in the fruits of Aron variety grown in point 1 (6.10%) and the lowest in the fruits of point 3 (4.40%) (Fig. 2). There were no significant differences in the fat content in the remaining varieties (5.30% in the Hugin variety and 5.60% in the Viking and Nero varieties.) According to the literature, the total fat content in aronia fruits reaches 0.14 g/100 g of fresh weight [17]. It was found that aronia seeds contain 19.3 g/kg of glyceride oil in which linoleic acid predominates.

Protein content in aronia fruits ranges from 3.1% in Viking variety to 5.6% in Hugin variety (Fig. 2). According to the literature, the protein content in fruits is 0.7 g/100 g fresh weight [17]. The composition of the fruit proteins is not yet clear, but according to 8 asparagine is a major component in the freshly squeezed juice [4].

Ash content ranges from 2.7% for Neo variety to 3.8% for Aron variety (Fig. 2). Fresh fruits have a mineral content (expressed as ash content) of 440 mg/100 g [17] and 580 mg/100 g [22].

IV. Conclusion

On the basis of the results we obtained, the following more important conclusions can be drawn:

1. Aronia is a culture that is tolerant to heavy metals and can be successfully grown on soils contaminated with heavy metals.
2. The increased content of heavy metals in the soil leads to less absorption of nutrients (Ca, Mg and P) in aronia fruits.
3. Soil pollution with heavy metals does not affect the quality of the fruits of Aron variety.

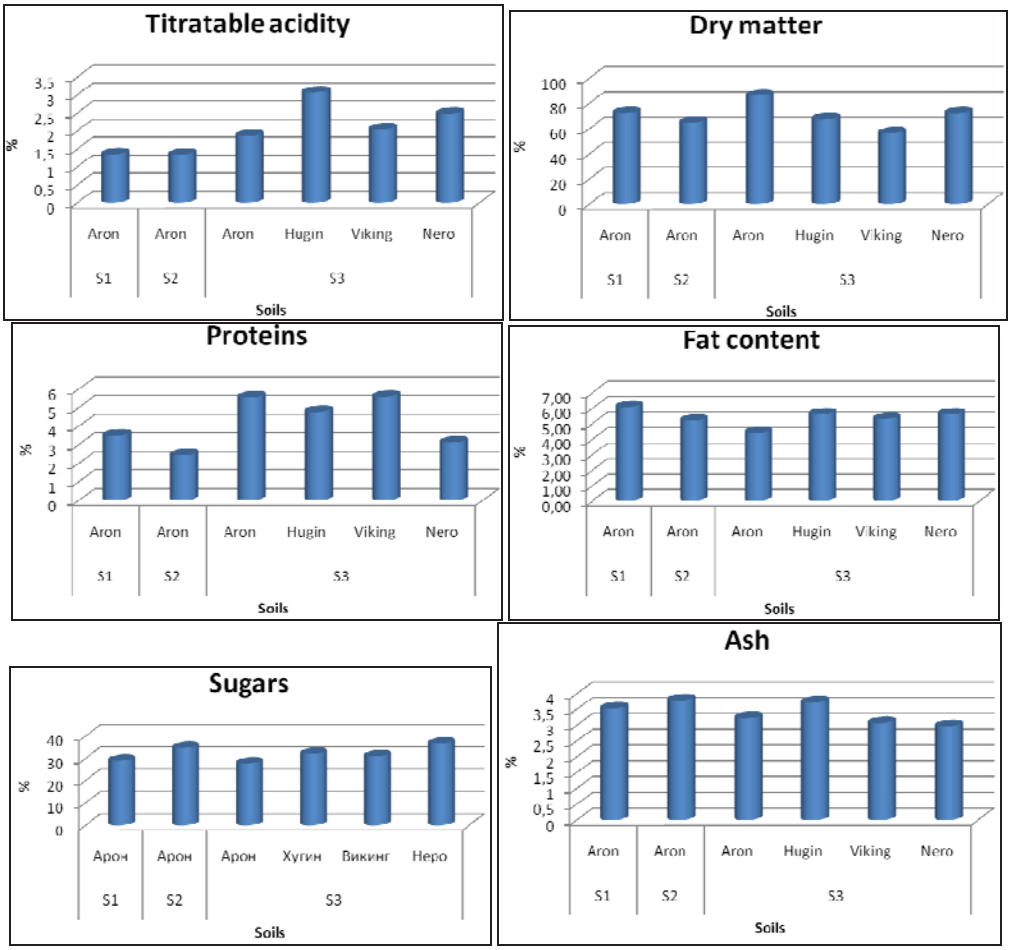

Fig. 2 Content of proteins, sugars, fat, ash and titrated acidity(%) in fruits of Aronia

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