

HEAVY METALS AND MACROELEMENTS IN ROWAN (*SORBUS AUCUPARIA* L.) FRUIT IN DIFFERENT FOREST ZONES OF THE BABIA GÓRA MT

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Abstract. Research on rowan fruit from northern slopes of the Babia Góra Mt revealed a decrease in the share of dry mass and an increase in the content of zinc parallel to increasing altitude. The average content of the elements: sodium, potassium, calcium, magnesium, iron, manganese, copper and lead in the fruit from the upper forest zone was smaller than in the fruit from the lower forest zone and the dwarf pine zone.

Key words: rowan fruit, share of dry mass, content of macro- and microelements, vegetation zones

INTRODUCTION AND AIM OF RESEARCH

Increasing contamination of natural environment does not spare specially protected areas, such as national parks. Due to their particular importance for science, education and recreation, they are researched on the character and intensity of anthropogenic factors which damage some elements of nature.

The research on selected species of mosses in the aspect of heavy metals being a threat to national parks, which was conducted in 1976 and repeated after 10 years, proves that the Babiogórski National Park is one of four most endangered parks in Poland [Grodzińska 1980, Grodzińska et al.1990]. The mountain range of the Babia Góra is particularly exposed to industrial emissions, which come here even from large distances, e.g. from the industrial regions of Slovakia and the Czech Republic (Ostrava), as well as from the Industrial Region of Silesia and Cracow. Relative altitude of the highest peaks, the dominant direction of winds and a high annual rainfall, usually positively correlated with the concentration of heavy metals in the environment, are additional factors.

Distinct vegetation zones of the Babia Góra Mt allow to conduct research within the borders of each zone and may later be used for comparison. This research was based

on the material from: lower forest zone, upper forest zone and dwarf pine zone. For this research, rowan (*Sorbus aucuparia* L.) was selected because its share is considerable in the plant communities of Babia Góra, especially in the upper areas [Babiogórski... 1986].

The aim of this research was to determine the level of heavy metals and some macrolelements in the fruit of this species depending on the vegetation zone. This work extends the research on chemical composition of rowan fruit from regions characterized by different anthropogenic influences [Barszcz 1998].

CHARACTERISTICS OF THE AREA AND STATIONS OF RESEARCH

Rowan fruit was collected mostly from the northern slopes of the Babia Góra Mt, from three forest zones, at the altitudes from 1030 to 1600 m. The share of rowan in stands and the intensity of its fructification clearly changed with the altitude of the collection point (called "station"): from rare occurrence and scarce fructification under the canopy of the stand, in the lower forest zone, to massive occurrence and abundant fructification in the highest parts of the upper forest zone, where rowan coexisted with dwarf pine. At even higher locations, rowan and dwarf pine together formed scrub and its fructification was less intensive than in lower areas. Fruit from higher parts of the upper forest zone and from the dwarf pine zone belonged to the "naked" variety of rowan (*S. aucuparia* L. var. *glabrata* Wimm. et Gr), which is one of constituents of characteristic phytocenoses, described by Celiński and Wojterski [1961] and Borysiak [1985].

The location of most research stations over the northern slope of the Babia Góra Mt imposed the following altitude borders for forest zones: the lower forest zone up to 1150 m, the upper forest zone up to 1390 m and the dwarf pine zone up to 1650 m [Celiński and Wojterski 1961]. In the lower forest zone, fruit was collected from two stands (stations 1 and 2), in the upper forest zone from four stands (stations 3 to 6), and in the dwarf pine zone from three locations (stations 7 to 9). Station 7, located on the ridge of the massif, was included in the dwarf pine zone [Celiński and Wojterski 1961, Pawłowski 1972]. Description of research stations [Babiogórski... 1986]:

Station 1. Compartment 18b; altitude 1050 m; steep northern slope; acid brown soil; mountain mixed coniferous forest; composition of species in the stand: 9 of spruce, 1 fir, 150 years old; small gap in the stand.

Station 2. Compartment 6d; altitude 1030 m; acid brown soil; mountain broadleaved forest; composition of species in the stand: 9 spruce, 1 beech 95 years old; valley – station near post-glacial lake.

Station 3. Compartment 20c; altitude 1175 m; steep northern slope; acid brown soil; mountain mixed coniferous forest; composition of species in the stand: spruce 60 years old, occasionally fir and beech; station under canopy of the stand.

Station 4. Compartment 23a; altitude 1240 m; steep northern slope; podzolic soil; high mountain coniferous forest; composition of species in the stand: 9 spruce, occasionally fir and beech 195 years old, 1 spruce, occasionally fir, beech, sycamore 135 years old; station under the canopy of the stand, near the stream.

Station 5. Compartment 22a; altitude 1350 m; valley; podzolic soil; high mountain coniferous forest; composition of species in the stand: 5 spruce, 205 years old, 5 spruce 175 years old; southern edge of the stand.

Station 6. Compartment 22i; altitude 1380 m; steep northern slope; podzolic soil; high mountain coniferous forest; composition of species in the stand: 6 dwarf pine 65 years old, 3 rowan 40 years old, 1 spruce 125 years old; near the border of the upper forest zone.

Station 7. Compartment 19h; altitude 1390 m; on the ridge between Kępa Mt and Sokolica Mt; podzolic soil; composition of species in the scrub; dwarf pine 80 years old.

Station 8. Compartment 22k; altitude 1460 m; very steep northern slope; podzolic soil; composition of species in the scrub: 8 dwarf pine 65 years old, 2 rowan 45 years old.

Station 9. Compartment 22s; altitude 1600 m; very steep northern slope; podzolic soil; composition of scrub: dwarf pine and rowan.

METHODOLOGY

At each research station, material was picked from one (if rowan was rare) to three trees. Fruit, several clusters from each station, was selected at random, from the southern side of the crown.

The following analyses for each station were conducted in the laboratory:

- 1) oven-dry mass share, with the temperature of drying 105°C [PN-90/A-75101/03],
- 2) content of 10 chemical elements in dry mass of fruit: sodium, potassium, calcium, magnesium, iron, manganese, zinc, copper, lead and cadmium.

The share of macro- and microelements was determined with the method of spectroscopic atomic absorption using the spectroscope of the Varian company, model Spectr AA-20. The average content of the elements was determined on the basis of 6 samples for each station and each chemical element. The material was not washed.

The results were elaborated statistically, calculating the average content of elements for each station and forest zone, as well as the variability coefficients (V%) for the features under research. In order to establish the significance of differences of the average content of chemical elements between forest zones, the single-factor analysis of variance, at significance level 0.05 was used.

RESEARCH RESULTS

The average content of chemical elements in rowan fruit is given in Table 1; additionally, changes of content of selected macro- and microelements are shown in Fig. 1. The share of oven-dry mass (in the whole material) amounted to about 20.47%. This feature had the smallest variability (coefficient of variability ranged from 8.3 to 10.9% depending on the altitude). The smallest share of oven-dry mass was noted at station 7, situated at a high altitude, and at two stations with very dry soil: near the post-glacial lake (station 2) and near the stream (station 4). This feature is related to altitude, with the share of dry mass decreasing as altitude increases. The difference in the content of

Table 1. Content of micro- and macroelements in dry mass of rowan fruit
Tabela 1. Zawartość makro- i mikroelementów w suchej masie owoców jarzębiny

| Station Stanowisko | Altitude Wysokość n.p.m. m | Share of dry mass Udział suchej masy % | Na % | K % | Ca % | Mg % | Fe ppm | Mn ppm | Zn ppm | Cu ppm | Pb ppm | Cd ppm |
|--------------------------|-------------------------------------|--|---------|--------|---------|---------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1 | 1 050 | 23.74 | 0.0037 | 2.75 | 0.55 | 0.26 | 68.33 | 337.67 | 19.13 | 12.10 | 4.82 | <0.5 |
| 2 | 1 030 | 19.63 | 0.0032 | 3.56 | 0.38 | 0.22 | 33.64 | 80.36 | 10.26 | 11.21 | 3.55 | <0.5 |
| Average Średnio V% | 21.68 | 0.00345 | 3.15 | 0.46 | 0.24 | 50.98 | 209.01 | 14.69 | 11.65 | 11.65 | 4.18 | |
| | 10.2 | 42.1 | 23.3 | 15.0 | 25.5 | 37.0 | 52.8 | 38.3 | 18.0 | 18.0 | 40.7 | |
| 3 | 1 175 | 21.69 | 0.0017 | 2.52 | 0.44 | 0.17 | 40.52 | 123.05 | 11.90 | 11.00 | 1.50 | <0.5 |
| 4 | 1 240 | 18.49 | 0.0020 | 2.59 | 0.34 | 0.16 | 38.00 | 308.30 | 16.12 | 5.67 | 2.77 | <0.5 |
| 5 | 1 350 | 22.19 | 0.0018 | 2.36 | 0.26 | 0.20 | 42.23 | 164.71 | 18.20 | 10.53 | 3.00 | <0.5 |
| 6 | 1 390 | 20.10 | 0.0009 | 2.64 | 0.47 | 0.19 | 37.91 | 89.52 | 17.00 | 6.27 | 1.40 | <0.5 |
| Average Średnio V% | 20.62 | 0.0016 | 2.53 | 0.38 | 0.38 | 0.18 | 39.66 | 171.39 | 15.80 | 8.37 | 2.17 | |
| | 8.3 | 39.9 | 7.4 | 37.0 | 11.2 | 19.0 | 48.4 | 16.3 | 16.3 | 27.4 | 45.2 | |
| 7 | 1 380 | 16.64 | 0.0013 | 2.59 | 0.39 | 0.18 | 37.33 | 165.00 | 18.36 | 11.58 | 1.90 | <0.5 |
| 8 | 1 460 | 20.68 | 0.0020 | 2.77 | 0.45 | 0.20 | 44.10 | 360.68 | 18.26 | 12.52 | 3.95 | <0.5 |
| 9 | 1 600 | 21.03 | 0.0064 | 3.09 | 0.51 | 0.21 | 47.51 | 216.45 | 20.44 | 11.50 | 1.80 | <0.5 |
| Average Średnio V% | 19.45 | 0.0032 | 2.82 | 0.45 | 0.45 | 0.20 | 42.98 | 262.84 | 19.02 | 11.87 | 2.55 | |
| | 10.9 | 50.6 | 9.1 | 34.7 | 9.6 | 40.5 | 42.6 | 25.2 | 25.2 | 5.5 | 50.8 | |

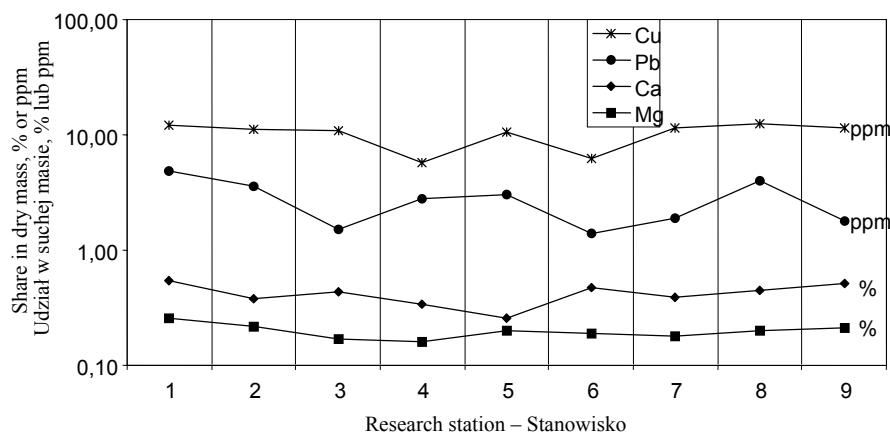


Fig. 1. Content of selected elements in rowan fruit from particular stations

Rys. 1. Zawartość wybranych pierwiastków w owocach jarzębiny z poszczególnych stanowisk

dry mass between material from different forest zones can be considered statistically significant (on the limit of significance level), because the value p is only slightly higher than the terminal value 0.05 (Table 2).

Table 2. Statistical assessment of differentiation of chemical composition in rowan fruit from three vegetation zones

Tabela 2. Statystyczna ocena zróżnicowania składu chemicznego owoców jarzębiny z trzech pięter roślinności

| Feature Cecha | F_{emp} | p | Result of statistical analysis Wynik analizy statystycznej |
|---|-----------|-------|---|
| Share of dry mass Udział suchej masy | 2.889 | 0.056 | ± |
| Sodium – Sód | 2.106 | 0.147 | – |
| Potassium – Potas | 2.142 | 0.145 | – |
| Calcium – Wapń | 5.367 | 0.013 | + |
| Magnesium – Magnez | 5.089 | 0.016 | + |
| Iron – Żelazo | 1.750 | 0.198 | – |
| Manganese – Mangan | 0.812 | 0.457 | – |
| Zinc – Cynk | 2.087 | 0.149 | – |
| Copper – Miedź | 19.033 | 0.000 | + |
| Lead – Ołów | 1.271 | 0.301 | – |

+ Means values for vegetation zones differ significantly.

– Means values for vegetation zones do not differ.

+ Wartości średnie dla pięter roślinności różnią się istotnie.

– Wartości średnie dla pięter roślinności nie różnią się.

The amount of sodium was characterized by relatively high variability (on average in the whole material about 42%). Clearly the highest content of this element was noted in fruit from the highest station 9, but at the same time the smallest content was also found at a high located station 6, near the upper border of the upper forest zone. The average content of sodium in dry mass of samples was 0.0026%.

Potassium and magnesium (on average: 2.76 and 0.20%) showed a small variability of content in the material under research. The highest percentage of these elements occurred: for potassium – at station 2, for magnesium – at station 1, in the lower forest zone.

The average level of calcium in the fruit amounted to about 0.42%, with the maximum at station 1 in the lower forest zone and the minimum at station 5 in the upper forest zone.

The amount of iron was determined at the level of about 43.29 ppm. Fruit from station 1 had evidently the highest content, fruit from station 2 – the smallest (both located in the lower forest zone).

The content of manganese and lead, which belongs to heavy metals, was characterized by the biggest variability coefficients. The average values of the variability coefficients ranged for manganese from 42.6 to 52.8% and for lead from 40.7 to 50.8%. Most of the manganese was discovered in the fruit from station 8, in the dwarf pine zone; the least in the fruit from stations 2 and 6. Most of the lead was discovered in the fruit from station 1; the least from station 6. The average amount of 205.08 ppm manganese and 2.74 ppm lead was determined in the material under research.

Zinc occurred on average in the amount of 16.63 ppm. The biggest amount of this element was contained in fruit from the highest located station 9, in the dwarf pine zone; the smallest - from the lowest located station 2, in the lower forest zone.

The level of copper (on average 10.26 ppm) changed only slightly. Most copper was noted in the sample from station 8 (the dwarf pine zone), the least from station 4 (the upper forest zone).

The level of cadmium was low, below 0.5 ppm. Using the equipment applied in this research, the amount of this element could not be determined with the accuracy bigger than given (Table 1).

Comparing, on the basis of a single-factor analysis of variance, the average content of macro- and microelements in fruit from the three distinguished zones, it was established that the material differs significantly only with respect to the level of calcium, magnesium and copper (Table 2).

The average level of most elements was higher within the lower forest zone and the dwarf pine zone than in the upper forest zone (Table 1). The exception is the amount of zinc, increasing with altitude. At the same time it has the opposite correlation to the share of oven-dry mass mentioned above. The variability of the share of dry mass and of the content of chemical elements within the upper forest zone is lower than the variability received in the dwarf pine zone and in the lower forest zone.

DISCUSSION

The data from papers by other authors may, to some extent, serve as a comparison for the results received in this work. In relation with the average content of dry mass in

rowan fruit from the whole of Poland, which is 27.5% [Grochowski 1990], this share in the material from the Babia Góra Mt was about 26% smaller. In comparison to fruit of this species in Kraków, the area round the Olkusz and from Myślenice Forest District [Barszcz 1998], the share of dry mass was here about 9% smaller. Therefore fruit from the Babia Góra Mt was characterized by relatively high moisture.

Due to lack of relevant comparative data concerning the level of potassium in rowan fruit from the area of Poland, the data was compared with that from Germany (for the sweet and bitter varieties), where the average content of this element was 0.35%, which was 8 times less than in this research [Eder et al. 1991].

Both in Polish and German research quoted here there is no data allowing to compare the level of sodium. The average amount of calcium in the samples is much higher than the average for Poland, quoted for rowan by Wnękowa [1976] at the level of 0.048%.

In comparison with the average level of magnesium for Poland in various plant species, contained within the scope of 0.3 to 1.0% fruit in this research has a very low level of this element. Relatively small content of magnesium may be a result of the action of acid rains on the exposed massif of the Babia Góra Mt [Kabata-Pendias and Pendias 1993]. However, a comparison of the share of this element with the results given by Eder et al. [1991] proves that its level is much higher in the fruit from the Babia Góra Mt.

The content of iron in rowan fruit examined by Wnękowa [1976] was on average 20 ppm. In the material from the Babia Góra Mt it was about twice higher, close to the level of iron from the area of the Olkusz [Barszcz 1998].

The amount of manganese, due to a lack of data on rowan for the area of Poland, was compared to the average content of this element in the fruit of various plant species from regions which are not industrially polluted, where it amounts to about 1 ppm in dry mass [Kabata-Pendias and Pendias 1993]. These authors maintain that for most plant species the concentration of manganese is toxic at the level of 500 ppm. In the fruit from the Babia Góra Mt the content of manganese is considerable and amounts to about 40% of the level regarded as toxic. Motowicka-Terelak [1987], in her research on toxicity of active manganese for plants, states that its harmful influence depends on the content of replaceable, i.e. phytoavailable magnesium in soil. As mentioned above, fruit in this research had very little magnesium, which may have influenced excessive accumulation of manganese, the element which may be antagonistic with relation to magnesium [Kabata-Pendias and Pendias 1993]. The presence of a large amount of manganese in this fruit may also be related to its occurrence, sometimes even at the level of over 400 ppm, in deeper layers of podzolic soils in the Babiogórski National Park [Panek 1987].

Other heavy metals, analysed in rowan fruit, and compared with their content in the dry mass of various plant species from regions not directly influenced by industry, do not exceed average values. For copper the average range of values is 5 to 20 ppm; for zinc 10 to 70 ppm; for lead up to 3 ppm [Kabata-Pendias and Pendias 1993]. Eder et al. [1991] determined less lead and much less zinc and copper (respectively from 4 to 7 times less) in the fruit from Germany as compared with the results of this research.

In comparison with earlier research [Barszcz 1998], the material analysed here contained about three times more copper than fruit from the area of Myślenice, Olkusz and Kraków. The content of zinc here was closed to that of Olkusz; the content of lead was a little lower than in the area of Olkusz and Kraków. A similarly small difference in the

content of zinc and lead in the juice of rowan fruit from Kraków (fruit was collected in a street) as compared with rowan juice from ecologically clean forest area near Gorlice (industrial damage zone 0 or I) was determined by Tuszyński and Zagól [1995]. Such a result suggests that rowan fruit cannot serve as a bioindicator of environmental pollution with heavy metals. The reason may be the existence of special natural physiological barrier which does not allow for excessive accumulation of heavy metals in such a specific organ of a plant as its fruit, even if the concentration of these metals in the environment is considerable. A tendency for a smaller content of lead, copper and zinc in fruit in comparison with their content in wood and leaves was shown on the example of hawthorn by Prączyński et al. [2002/03]. On the other hand, rowan leaves, which gather large amounts of metallic dust on their surface, are regarded as highly useful for monitoring purposes [Supuka 1980, Vike et al. 1995] and for the assessment of the stability of stands threatened by industrial pollution [Olszewski 2003].

The research on the contamination of soil in the Babiogórski National Park with heavy metals proved a considerable concentration of lead, zinc and copper of anthropogenic origin, especially in surface layers of podzolic soils [PANEK 1987]. Against the background of average values given for unpolluted regions of Poland, Panek states that the Park is endangered due to the accumulation of these metals in soil. Most heavy metals were noted by that author in the soils of the dwarf pine zone, which are under the far-reaching influence of industry, as well as in the soils of the lower forest zone (a possible local influence of the road from Zawoja to Zubrzyca). A significant influence of traffic pollution on the content of heavy metals in forest fruit was also noted by Curzydło [2001]. These results are to a large extent in accordance with the average content of zinc, lead and copper in the rowan fruit: the analysis described in this paper determined the largest concentration of zinc - in the material from the dwarf pine zone, and of lead and copper - in the material from both the lower forest zone and the dwarf pine zone.

Looking at the changes of the level of macro- and microelements in fruit at different research stations, one may observe tendencies to a positive or negative correlation between the content of certain chemical elements (Fig. 1). The positive correlation was shown at some stations by: copper with lead and magnesium with copper. The negative correlation was discovered between the level of calcium and lead, which may indicate their antagonistic interaction [Kabata-Pendias and Pendias 1993]. It should be pointed out that in the present research, in the group of three out of all elements shown on the graph, i.e. calcium, magnesium and copper, there were statistically significant differences depending on a forest zone (Table 2).

SUMMING UP AND CONCLUSIONS

1. The average level of macro- and microelements in rowan fruit from the Babia Góra Mt was differentiated depending on a forest zone. As a rule, the smallest content of elements and, at the same time, the smallest variability of results was noted in the material from the upper forest zone. Exceptionally, the average content of zinc increased in the direction from the lower forest zone to the dwarf pine zone, and the share of dry mass in fruit had the opposite tendency. The material from particular vege-

tation zones differed significantly with relation to the content of calcium, magnesium and copper.

2. In comparison with rowan fruit from other regions of Poland, material in this research was characterized by higher moisture and a higher content of calcium, iron and copper. Against the background of research done by other authors, analyses also showed considerable amounts of manganese in the material.

3. The level of zinc and lead in the fruit from the slopes of the Babia Góra Mt is only a little lower than in the material from the area of Olkusz and Kraków. A relatively small difference in the content of the metals mentioned above between the fruit from the Babia Góra Mt and the fruit from regions under direct influence of industry confirms the results of research carried out by other authors which indicates that this National Park is threatened by anthropogenic influences. However, such a result may also point out the fact that rowan fruit is not useful for the purposes of monitoring of environmental pollution caused by the chemical elements mentioned above.

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METALE CIĘŻKIE I MAKROELEMENTY W OWOCACH JARZĘBU POSPOLITEGO (*SORBUS AUCUPARIA* L.) Z RÓŻNYCH PIĘTER ROŚLINNYCH BABIEJ GÓRY

Streszczenie. Badania owoców jarzębiny z północnych stoków Babiej Góry wykazały spadek udziału suchej masy oraz wzrost zawartości cynku w miarę zwiększania się wysokości nad poziomem morza. Średnia zawartość takich pierwiastków, jak sód, potas, wapń, magnez, żelazo, mangan, miedź i ołów była w owocach ze strefy regla górnego mniejsza niż w strefie regla dolnego i w piętrze kosodrzewiny.

Słowa kluczowe: owoce jarzębiny, udział suchej masy, zawartość makro- i mikroelementów, piętra roślinne

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