



ORIGINAL PAPER

TIME-RELATED VARIABILITY OF THE MINERAL CONTENT IN BIRCH TREE SAP

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ABSTRACT

Minerals are among the most important substances promoting the beneficial effect of tree sap on a human body. However, the composition of tree saps is characterised by high intra- and interspecies variability and it is also known to vary in time even when collected from trees of the same species. The aim of this work was to evaluate the time-related variability of the mineral content in birch tree sap, to prove dependencies between the mineral composition and basic physical parameters of tree saps, and to refer the results obtained in our study to the Polish nutritional standards. Based on the results, it can be concluded that there is no point in time when birch sap invariably achieves superior nutritive values. This is proven by the fact that two of the three tested birch trees had a higher content of minerals at the beginning of sap collection, while the remaining one produced better sap at the end of the experiment. The differences in the mineral composition of tree saps observed during the two-week study raise doubt about the nutritional benefits of their content. For example, one liter of sap collected during two weeks from the three tested birches supplied from 8.49 to 26.34%, 0.9 to 2.80% and 9.17 to 20.23% of the adequate intake of potassium defined in the *Nutritional standards for the Polish population* (2013). For zinc, the recommended dietary allowance value based on the *Nutritional standards for the Polish population* (2013) was covered by one liter of sap in the following ranges: from 0 to 2.11%, from 0.85 to 21.50% and from 7.34 to 15.63%. Moreover, it is impossible to estimate the nutritional value of tree saps, understood as the mineral content, from the physical parameters of birch saps. The values of the examined parameters did not correspond reliably to the mineral content. Nonetheless, electrolytic conductivity may reflect more faithfully the nutritional benefits. The higher the EC in the saps from two out of the three birch trees tested, the higher the expected concentration of minerals important for humans, i.e. calcium, zinc and potassium.

Keywords: tree saps, minerals, time-related variability, food standards, nutritional benefits.

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INTRODUCTION

The health-promoting properties of tree saps have been described in numerous publications (CHOI et al. 2005, QADIR et al. 2007, LEE et al. 2009, PEEV et al. 2010), largely confirming their broad applicability in folk medicine in Asia, Europe and North America (SVANBERG et al. 2010, PAPP et al. 2014, RASTOGI et al. 2015). Minerals are among the most important substances promoting the beneficial effect of tree sap on a human health. Tree saps most frequently contain potassium, magnesium, calcium and zinc. Manganese and copper can be found as well, although in lower concentrations (VIŠKELIS, RUBINSKIENĖ 2011, JEONG-JEONG et al. 2012, KŪKA et al. 2013, BILEK et al. 2015a, 2016a). The mineral composition of tree saps, including the high content of zinc, copper and manganese, may be a factor contributing to the health-promoting activity, often mentioned in ethnomedical reports, i.e. tree sap used in treatment of infectious diseases and immunodeficiencies, or to improve the condition of hair, skin and nails, both applied internally and externally (SVANBERG et al. 2010, PAPP et al. 2014).

According to the studies by HOLGATE (1950), LAROCHELLE et al. (1998), MOON et al. (2004) and JEONG et al. (2011), the composition of tree saps is characterised by high intra- and interspecies variability. Changes in the composition have been detected even in a single location, which can make it more difficult for consumers to obtain any nutritional benefits when collecting and consuming saps from random trees, without paying attention to the parameters likely to affect the quality of sap (BILEK et al. 2015a, 2016a). It is also known that tree sap composition varies in time, including changes in the content of sugars (KALLIO, AHTONEN 1987a, JEONG-JEONG et al. 2012), amino acids (AHTONEN, KALLIO 1989) and organic acids (KALLIO, AHTONEN 1987b, JEONG-JEONG et al. 2012), minerals (HAJRU, HULDÉN 1990, JEONG-JEONG et al. 2012) or in the physical parameters, e.g. pH, acidity and ash (ESSIAMAH 1980, JEONG-JEONG et al. 2012).

The aim of this work was to evaluate time-related variability of the mineral content in birch tree sap, to prove dependencies between the mineral composition and basic physical parameters of tree saps, and to refer the results obtained to the Polish nutritional standards.

MATERIAL AND METHODS

Tree sap was collected in Niwiska, a village situated on Kolbuszowski Plateau. The tree sap collection was performed according to the guidelines contained in YOON et al. (1992). The sap was collected from three trees of *Betula pendula* Roth species for 15 days, starting on the fifth day of sap flow. The birch sap was collected continuously, measuring its daily volume.

The physical parameters were analysed directly after the sap had been collected. The dry matter content was measured with a moisture balance RadWag, at the temp. of 90°C to prevent thermal decomposition of fructose. A multi-parameter meter (Hanna Instrument 9811-5) was used to determine the pH and electrolytic conductivity. The refraction value was determined at 21°C using a digital refractometer (Hanna Instrument 96801). Moreover, during the fifteen days of tree sap collection, the air temperature was measured twice a day (at midday and at midnight) with a ThermaQ thermometer (Figure 1).

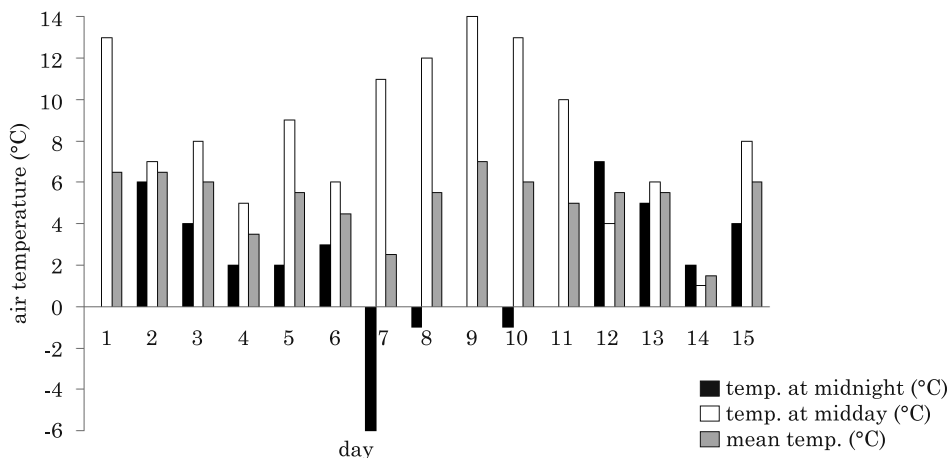


Fig. 1. Air temperature during the sap collection period

The mineral content was determined after the whole batch of study material was collected. Fresh birch sap was stored at -21°C and then the whole batch was transported to the laboratory of the Analytical Chemistry Division of the Medical University in Lublin, where the mineral composition was analysed.

The content of potassium, sodium, calcium, magnesium and zinc was determined using the flame atomic absorption spectrometry technique (Table 1).

Table 1

The validation parameters for Flame Technique of Atomic Absorption Spectrometry analysis

| Ele- ment | Line (nm) | Flow of carrier gases (L h ⁻¹) | Burner height (mm) | Conc. range (mg dm ⁻³) | Correlation coeff. (<i>R</i>) | Precision (%RSD) | LOD (mg dm ⁻³) | LOQ (mg dm ⁻³) |
|--------------|--------------|---|--------------------------|--|------------------------------------|---------------------|-------------------------------|-------------------------------|
| Zn | 213.86 | 50 | 6 | 0-1 | 0.9999 | 0.6-1.4 | 0.062 | 0.235 |
| Mg | 285.21 | 70 | 6 | 0-0.5 | 0.9999 | 0.4-2.0 | 0.035 | 0.127 |
| K | 766.49 | 80 | 8 | 0-0.5 | 0.9999 | 0.2-0.9 | 0.033 | 0.101 |
| Ca | 422.63 | 100 | 7 | 0-5 | 0.9999 | 0.4-1.2 | 0.010 | 0.038 |
| Na | 588.99 | 90 | 6 | 0-1.5 | 0.9998 | 0.4-0.9 | 0.025 | 0.081 |

LOD – the Limit of Detection, LOQ – the Limit of Quantification, RSD – relative Standard Deviation

Stock solutions in a concentration of 0.5 mg dm^{-3} for magnesium, 0.5 mg dm^{-3} for potassium, 1.5 mg dm^{-3} for sodium, 5 mg dm^{-3} for calcium, 1 mg dm^{-3} for zinc were prepared by dilution of standard solutions in the concentration of 1000 mg dm^{-3} (Merck, Germany) in 0.5% nitric acid, prepared by dilution of 65% Suprapur nitric acid (Merck, Germany) in deionised water with an Ultrapure Millipore Direct-Q-R 3UV (Merck, Germany) of the resistivity $18.2 \text{ M}\Omega \cdot \text{cm}$.

The content of minerals was determined by the flame technique of atomic absorption spectrometry on a High-Resolution Continuum Source Atomic Absorption Spectrometer ContrAA 700 (Analytik Jena, Germany). The calibration curves for the minerals were selected by decomposition of residues. 20% KCl as an ionization buffer was added to calibration standard solutions and to each sample, while 20% NaCl was used as an ionization buffer for the determination of potassium. The final ionization buffer concentration in a sample was 0.1%. The dilution factor was chosen automatically by an auto-sampler.

The copper and iron content was determined using the graphite furnace technique of atomic absorption spectrometry (Table 2). Stock solutions in the

Table 2

The validation parameters for Electrothermal Technique of Atomic Absorption Spectrometry analysis

| Element | Line (nm) | Drying temp. (°C) | Pyrolysis temp. (°C) | Atomization temp. (°C) | Conc. range ($\mu\text{g dm}^{-3}$) | Correlation coeff. (<i>R</i>) | Precision (%RSD) | LOD ($\mu\text{g dm}^{-3}$) | LOQ ($\mu\text{g dm}^{-3}$) |
|---------|-----------|-------------------|----------------------|------------------------|---------------------------------------|---------------------------------|------------------|-------------------------------|-------------------------------|
| Cu | 324.75 | 110 | 1050 | 1950 | 0-10 | 0.9998 | 0.2-2.6 | 0.127 | 0.472 |
| Fe | 248.32 | 110 | 1150 | 2100 | 0-30 | 0.9999 | 0.4-1.8 | 1.309 | 4.129 |

Explanations – see Table 1

concentrations of $10 \mu\text{g dm}^{-3}$ for copper and $30 \mu\text{g dm}^{-3}$ for iron were prepared by dilution of the standard solutions in the concentration of 1000 mg dm^{-3} (Merck, Germany) in 0.5% nitric acid, prepared by dilution of 65% Suprapur nitric acid (Merck, Germany) in deionised water by an Ultrapure Millipore Direct-Q-R 3UV (Merck, Germany) of the resistivity $18.2 \text{ M}\Omega \cdot \text{cm}$.

The content of copper and iron was determined by the electrothermal technique of atomic absorption spectrometry with atomization in a L'vov platform graphite cuvette using a High-Resolution Continuum Source Atomic Absorption Spectrometer ContrAA 700 (Analytik Jena, Germany). The calibration curves for the minerals were selected by decomposition of residues. The dilution factor of analysed samples was chosen automatically by an autosampler. A $25 \mu\text{L}$ each sample solution with $5 \mu\text{L}$ of $\text{Pd}(\text{NO}_3)_2/\text{Mg}(\text{NO}_3)_2$ matrix modifier was injected into the furnace.

Determination of the content of minerals was carried out in triplicate, after filtration through a MCE $0.45 \mu\text{m}$ syringe filter. In order to obtain the

results within the linear range of the standard curve, dilution of the samples was performed.

The results were referred to the *Nutritional standards for the Polish population* for electrolytes and minerals (JAROSZ 2012). Comparisons with the Recommended Dietary Allowance as well as Adequate Intake for an adult woman relative to one liter of birch saps were made.

The results were processed with statistical analysis software Statistica10 (StatSoft, Inc.) and Microsoft Excel 2007 (Microsoft Corporation). Two-way analysis of variance (ANOVA) and Least Significant Difference (LSD) tests were performed with the statistical significance level set at 5% ($\alpha = 0.05$).

RESULTS AND DISCUSSION

The average values of the physical parameters of birch sap for the whole examination period are comprised in Table 3, while Figures 2-6 illustrate changes in values of the parameters during the two-week examination period.

Table 3

The average values of the physical parameters of birch tree saps

| Birch | Daily sap volume (dm ³ day ⁻¹) | Total sap volume (dm ³) | Dry matter (%) | Refraction value (°Brix) | Electrolytic conductivity (μS cm ⁻¹) | pH |
|-------|---|-------------------------------------|--------------------------|--------------------------|--|--------------------------|
| A | 2.00 ^a ± 1.35 | 29.95 ^a | 0.38 ^a ± 0.06 | 0.58 ^a ± 0.10 | 156.3 ^a ± 38.6 | 6.41 ^a ± 0.38 |
| B | 1.89 ^a ± 1.20 | 28.14 ^a | 0.65 ^c ± 0.11 | 0.93 ^b ± 0.09 | 417.0 ^c ± 40.7 | 6.22 ^a ± 0.17 |
| C | 2.84 ^a ± 1.67 | 42.62 ^b | 0.49 ^b ± 0.07 | 0.64 ^a ± 0.09 | 231.0 ^b ± 26.7 | 6.26 ^a ± 0.24 |

Different letters in a column indicate significant differences between individual trees at significance level $\alpha = 0.05$.

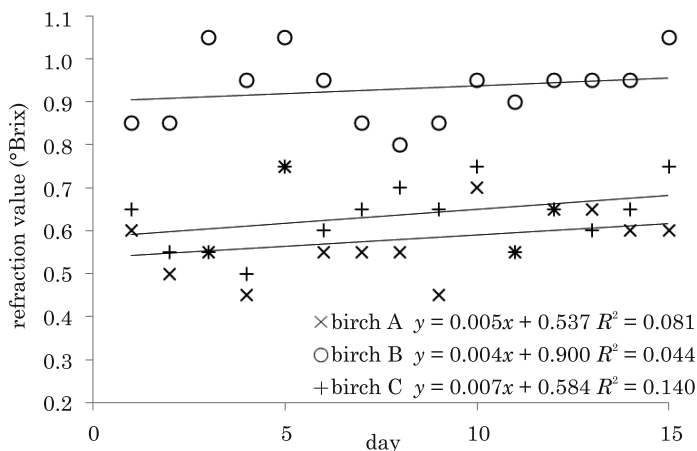


Fig. 2. Time-related variability of refraction values in the tree saps

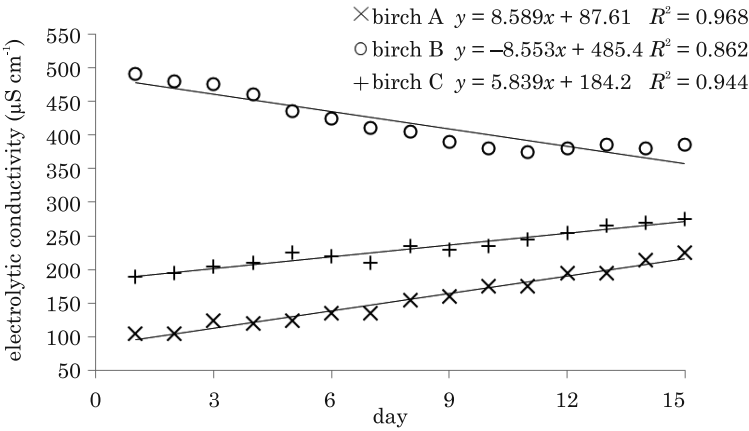


Fig. 3. Time-related variability of electrolytic conductivity in the tree saps

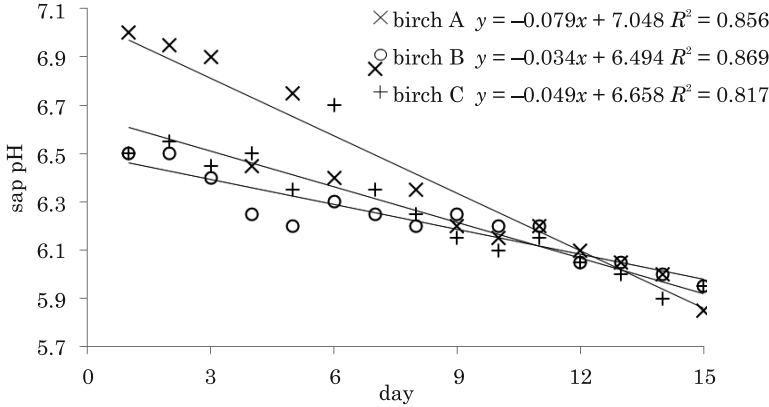


Fig. 4. Time-related variability of pH in the tree saps

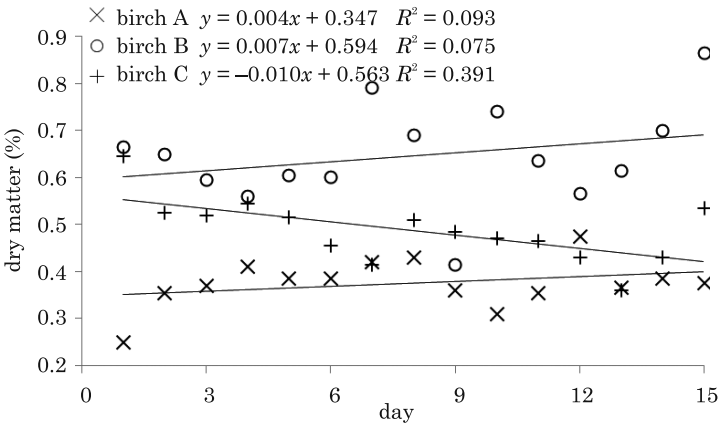


Fig. 5. Time-related variability of dry matter in the tree saps

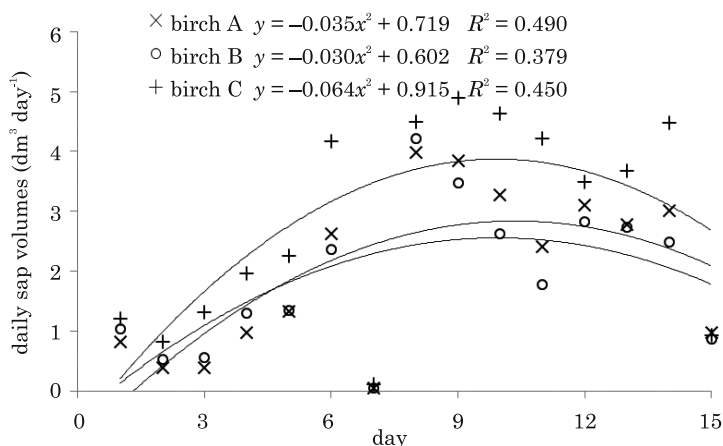


Fig. 6. Time-related variability of daily sap volume in the tree saps

Two-way variance analysis revealed significant influence of an individual tree on the content of all minerals in sap except for iron. It did not, however, confirm any consistent influence of a sap collection date on the mineral content. Individual differentiation between the three birch trees is proven by the fact that they made a single, homogeneous group with respect to the average iron content in sap, while creating three homogeneous groups for the magnesium content and two homogeneous groups for the other minerals (Table 4).

Figures 7-13 illustrate the time-related variability of the mineral content in the saps of three birch trees. The dominant mineral in birch sap collected from each of the three trees was potassium, whose content ranged from 76.4 mg dm⁻³ in birch tree B to 624 mg dm⁻³ in birch tree C (Figure 8). Its content made up from 59.56 (tree B) to 96.84% (tree C) of the total content of the determined minerals. The second most abundant mineral in the sap of birch trees A, B and C was calcium (Figure 10), constituting from 2.61 (tree A) to 34.03% (tree B). The third most abundant mineral in each of the examined saps was magnesium (Figure 9), making up from 0.52 (tree A) to 5.69% (tree B) of the determined minerals. The least abundant mineral of all the examined minerals in birch sap of each tree was copper (Figure 12), with an average value ranging $0.39 \pm 0.62 \mu\text{g dm}^{-3}$ (tree B) to $4.42 \pm 1.73 \mu\text{g dm}^{-3}$ (tree A), i.e. less than 0.001% of the determined minerals.

The lowest average total of all the minerals, amounting to $128.26 \pm 38.52 \text{ mg dm}^{-3}$, was characteristic of birch tree B (Figure 14). This total amount corresponded to hardly more than 2% of dry matter. The highest average total of the determined minerals ($657.68 \pm 163.02 \text{ mg dm}^{-3}$) was recorded in sap from tree A. It reached above 13.5% of dry matter.

The date of collecting birch sap was not found to have any consistent influence on the mineral content and it had different effects on sap from the three trees. Changes in the sodium content of sap are best described by the

Table 4

Mineral content in the birch tree saps

| Mineral | Birch | | | | | | |
|--|------------------------------|--------|------------------------------|--------|------------------------------|--------|----------------------------|
| | A | | B | | C | | Mean |
| | mean and SD | CV (%) | mean and SD | CV (%) | mean and SD | CV (%) | |
| Na (mg dm ⁻³) | 0.159 ^b ± 0.055 | 34.670 | 0.160 ^b ± 0.100 | 62.740 | 0.098 ^a ± 0.024 | 24.589 | 0.139 ± 0.072 51.836 |
| K (mg dm ⁻³) | 540.76 ^b ± 221.76 | 41.009 | 76.40 ^a ± 21.53 | 28.184 | 624.22 ^b ± 156.58 | 25.084 | 413.793 ± 88.089 69.621 |
| Mg (mg dm ⁻³) | 2.901 ^a ± 1.461 | 50.379 | 7.298 ^c ± 2.439 | 33.414 | 4.513 ^b ± 1.139 | 25.239 | 4.904 ± 2.522 51.422 |
| Ca (mg dm ⁻³) | 14.552 ^a ± 7.478 | 51.390 | 43.643 ^b ± 14.466 | 33.147 | 27.933 ^a ± 6.505 | 23.287 | 28.709 ± 15.569 54.231 |
| Zn (mg dm ⁻³) | 0.014 ^a ± 0.044 | 315.75 | 0.740 ^b ± 0.449 | 60.661 | 0.906 ^b ± 0.203 | 22.446 | 0.553 ± 0.481 86.917 |
| Cu (µg dm ⁻³) | 4.42 ^b ± 1.73 | 39.235 | 0.39 ^a ± 0.62 | 159.86 | 0.87 ^a ± 0.83 | 95.332 | 1.89 ± 2.14 113.39 |
| Fe (µg dm ⁻³) | 10.00 ^a ± 3.08 | 30.797 | 21.84 ^a ± 48.95 | 224.17 | 9.24 ^a ± 4.65 | 50.300 | 13.69 ± 28.40 207.35 |
| The sum of the minerals (mg dm ⁻³) | 558.40 ^b ± 228.93 | 40.994 | 128.26 ^a ± 38.52 | 30.046 | 657.68 ^b ± 163.02 | 24.775 | 448.11 ± 282.14 62.842 |
| The sum of the minerals as % of dry matter | 15.17 ^b ± 6.49 | 42.795 | 2.02 ^a ± 0.64 | 31.755 | 13.51 ^b ± 2.91 | 21.529 | 10.24 ± 7.15 69.793 |

Different letters in rows indicate significant differences between individual at significance level $\alpha = 0.05$, SD – Standard Deviation, CV – Coefficient of Variation.

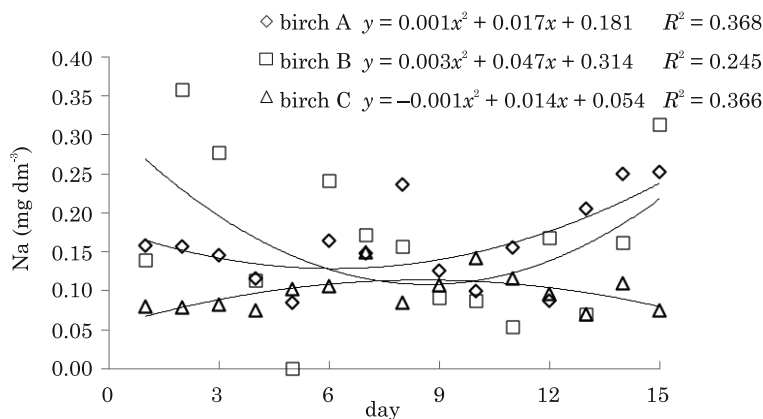


Fig. 7. Time-related variability of sodium content in the tree saps

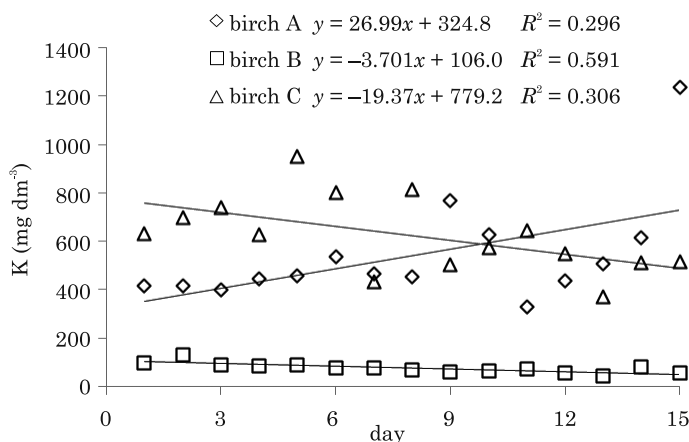


Fig. 8. Time-related variability of potassium content in the tree saps

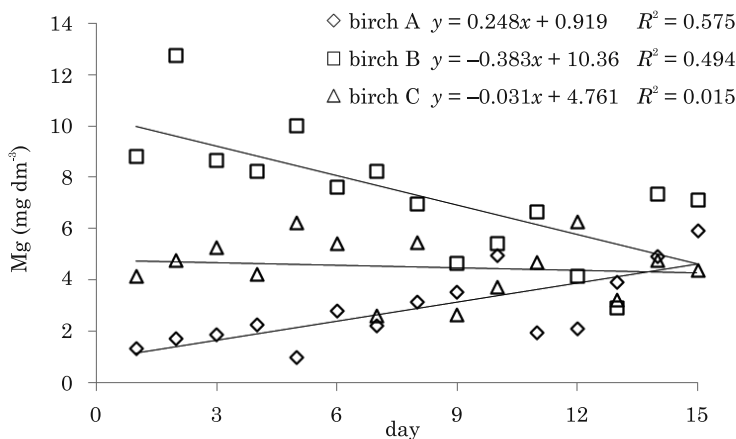


Fig. 9. Time-related variability of magnesium content in the tree saps

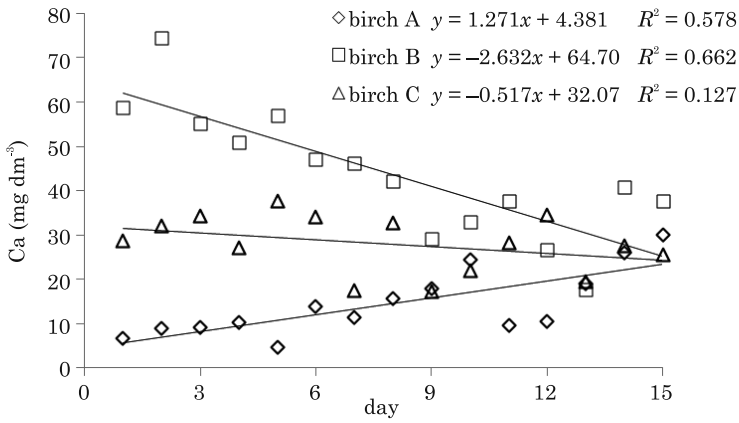


Fig. 10. Time-related variability of calcium content in the tree saps

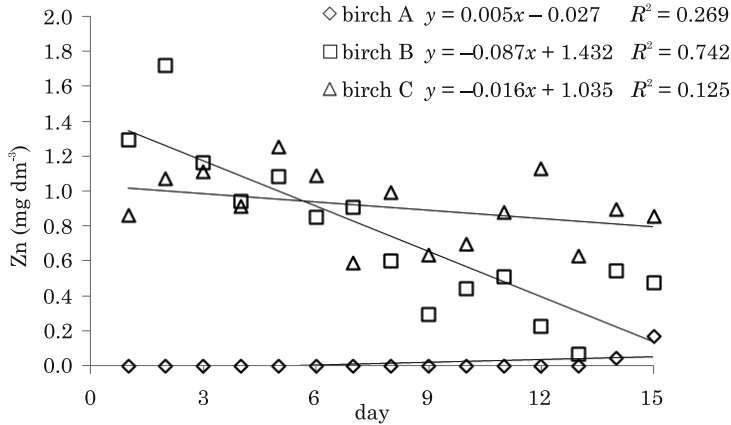


Fig. 11. Time-related variability of zinc content in the tree saps

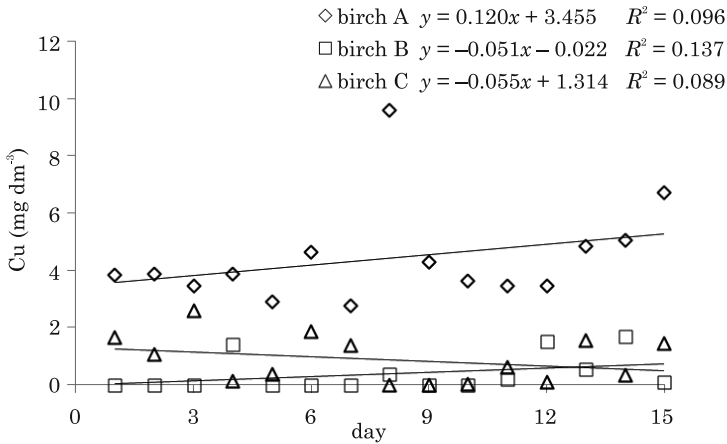


Fig. 12. Time-related variability of copper content in the tree saps

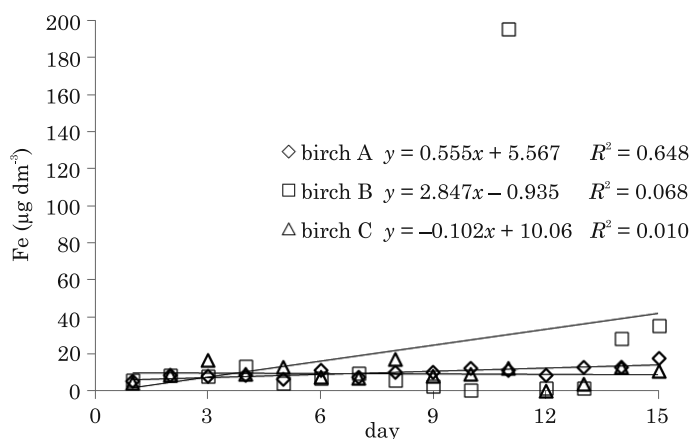


Fig. 13. Time-related variability of iron content in the tree saps

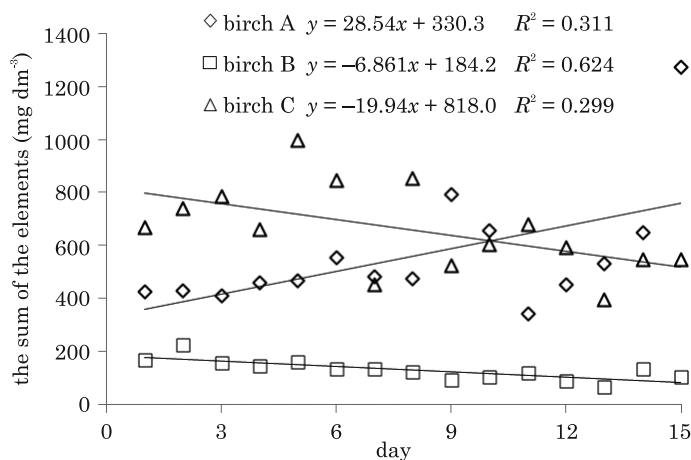


Fig. 14. Time-related variability of mineral content in the tree saps

polynomial of 2nd degree, with the minimum for trees A and B (about 5th and 8th day, respectively), and with the maximum for tree C (on about 9th day).

The influence of a sap collection date on the content of the other minerals is best described by a linear function. In tree A sap, the content and total of minerals grew with the time of collection, while the same values decreased for tree C sap over time. For tree B sap, the copper and iron content tended to grow in time while that of the other minerals and their total fell down. To sum up, the total of all minerals in birch A sap increased by more than 28.5 mg dm⁻³ a day, while for tree B and C saps it fell down by 6.803 and 19.93 mg dm⁻³, respectively.

The mineral content in birch sap was correlated positively with the temperature at night, except for sodium in tree C, magnesium and zinc in tree B, and the total content of minerals for both trees (Table 5). For tree A, the

Table 5

Correlation coefficients for the mineral content in birch tree saps with air temperature

| Mineral | Temperature at midnight | | | Temperature at midday | | | Mean temperature | | |
|--|-------------------------|--------|--------|-----------------------|---------|---------|------------------|---------|---------|
| | birch | | | | | | | | |
| | A | B | C | A | B | C | A | B | C |
| Na (mg dm ⁻³) | 0.020 | 0.369* | -0.684 | -0.219 | -0.250 | 0.298 | -0.244 | 0.091 | -0.371* |
| K (mg dm ⁻³) | 0.079 | 0.054 | 0.093 | 0.041 | -0.035 | 0.092 | 0.135 | 0.015 | 0.211 |
| Mg (mg dm ⁻³) | 0.007 | -0.014 | 0.511* | -0.107 | -0.022 | -0.408* | -0.122 | -0.042 | 0.052 |
| Ca (mg dm ⁻³) | 0.004 | 0.002 | 0.479* | -0.120 | 0.026 | -0.329 | -0.142 | 0.033 | 0.114 |
| Zn (mg dm ⁻³) | 0.186 | -0.002 | 0.536* | -0.170 | 0.059 | -0.376 | -0.006 | 0.070 | 0.117 |
| Cu (µg dm ⁻³) | 0.033 | 0.001 | 0.537* | -0.127 | -0.022 | -0.392 | -0.119 | -0.026 | 0.099 |
| Fe (µg dm ⁻³) | 0.008 | 0.316 | 0.167 | 0.055 | -0.741* | -0.066 | 0.075 | -0.561* | 0.099 |
| The sum of the elements (mg dm ⁻³) | 0.200 | -0.132 | -0.214 | -0.220 | 0.028 | 0.125 | -0.053 | -0.108 | -0.078 |
| The sum of the minerals as % of dry matter | 0.077 | 0.031 | 0.113 | 0.035 | -0.011 | 0.071 | 0.125 | 0.019 | 0.207 |

* Statistically significant at $\alpha = 0.05$.

correlations are weak and have no statistical significance. For tree B, the content of sodium and iron was slightly *albeit* significantly correlated with the temperature at night, although the correlations for the content of the other minerals were weak. The best correlation with the temperature at night was detected for tree C sap, with a high correlation for sodium and moderate ones for magnesium, calcium, zinc and copper.

The birch sap mineral content was correlated with the air temperature at midday and the average daily temperature less strongly than with the midnight temperature. Significant correlations with the temperature at midnight were detected: for tree B sap – only the iron content (high), for tree C sap – magnesium content (moderate) and calcium, zinc and copper content (low). It should be mentioned that those were negative correlations. Significant correlations with the average daily temperature were detected for the iron content in tree B sap and sodium content in tree C sap. Those were negative correlations, moderate in the former case and low in the latter one.

A, B and C trees were characterised by highly different relationships of the determined physical parameters of their saps with the mineral content expressed by the Pearson's correlation coefficients (Table 6). The strongest correlation of the mineral content was detected for the electrolytic conductivity and pH value in trees A and B. For the electrolytic conductivity in tree A,

Table 6

Correlation coefficients for the mineral content in birch tree saps with physical parameters

| | Birch | Mineral | | | | | | | | |
|--|-------|------------------------------|-----------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|---|--|
| | | Na (mg dm ⁻³) | K (mg dm ⁻³) | Mg (mg dm ⁻³) | Ca (mg dm ⁻³) | Zn (mg dm ⁻³) | Cu (µg dm ⁻³) | Fe (µg dm ⁻³) | the sum of the elements (mg dm ⁻³) | the sum of the minerals as % of dry matter |
| Dry matter (%) | A | -0.011 | -0.046 | -0.027 | -0.028 | 0.011 | 0.195 | 0.063 | -0.046 | -0.348 |
| | B | 0.327 | 0.018 | 0.192 | 0.091 | 0.069 | -0.153 | 0.084 | 0.058 | -0.398 |
| | C | -0.389 | 0.458* | 0.180 | 0.340 | 0.315 | 0.107 | 0.225 | 0.456* | -0.389 |
| Refraction (°Brix) | A | -0.144 | 0.031 | 0.101 | 0.098 | 0.081 | -0.133 | 0.068 | 0.034 | 0.083 |
| | B | 0.043 | -0.161 | -0.018 | -0.063 | -0.087 | 0.084 | -0.037 | -0.116 | -0.119 |
| | C | 0.300 | 0.048 | 0.051 | -0.063 | -0.079 | -0.278 | 0.074 | 0.044 | 0.300 |
| Electrolytic conductivity (µS cm ⁻¹) | A | 0.464* | 0.582* | 0.789* | 0.793* | 0.582* | 0.338 | 0.823* | 0.595* | 0.484* |
| | B | 0.349 | 0.797* | 0.747* | 0.849* | 0.894* | -0.252 | -0.303 | 0.823* | 0.825* |
| | C | -0.003 | -0.419* | 0.041 | -0.190 | -0.189 | -0.280 | -0.026 | -0.410* | -0.003 |
| pH | A | -0.358 | -0.565* | -0.786* | -0.773* | -0.474* | -0.393 | -0.825* | -0.577* | -0.467* |
| | B | 0.232 | 0.751* | 0.626* | 0.743* | 0.806* | -0.498* | -0.121 | 0.748* | 0.795* |
| | C | -0.116 | 0.582* | 0.176 | 0.392 | 0.391 | 0.388 | 0.047 | 0.576* | -0.116 |

* Statistically significant at $\alpha = 0.05$.

those were positive and significant correlations, except for the copper content, whose correlation coefficient was not significant. Regarding tree B, except for positive correlations, negative correlation coefficients were recorded between conductivity and the content of copper and iron. The electrolytic conductivity of tree C sap was negatively correlated with its mineral content. It is worth noticing that only the correlations between electrolytic conductivity and the potassium content as well as the total of all minerals in tree C sap were significant. Birch tree A sap had a pH value that was correlated negatively with the sap content of all the determined minerals. Those were significant correlations, except for sodium and copper. For trees B and C, there were positive correlations for the analysed parameters, except for copper and iron in tree B sap and sodium in tree C sap. Similar differences between the three trees were found in respect of the mineral content correlation with the dry matter and refraction value. However, we should point to the significant differences between these two parameters, in particular to the fact that the value of refraction is higher than dry matter, while it should be the opposite, due to the presence of minerals and organic acids. To sum up, those are weak correlations, which is proven by the fact that only the correlations between dry matter and the potassium content as well as total minerals in tree C sap are significant.

The time-related variability of tree sap composition can be analysed from different angles. The existing studies of the seasonal variability of tree saps focused mainly on economic and practical aspects (KALLIO, AHTONEN 1987*a, b*, AHTONEN, KALLIO 1989). In the context of birch syrup manufacture profitability, the sugar content in birch sap from Finland (KALLIO, AHTONEN 1987*a*) was examined in a one-month study. The recorded differences in the order of several to several dozen times primarily affect the economy as they cause an analogous decrease or increase in the profitability of manufacture of birch syrup, produced by evaporation of birch sap. Differences recorded for one tree concerning the total sugar content in tree sap collected within one week were very high. For three silver birch trees and three downy birch trees studied by the cited authors, the total one-week content of glucose in the collected sap ranged from 14.1 to 97.5 g for silver birch and from 5.1 to 125.9 g for downy birch, while that of fructose, for the same individual trees, varied from 12.8 to 77.3 g and from 7.7 to 115.6 g, respectively. The highest sugar output for every tree was recorded in the third and fourth week of collection (KALLIO, AHTONEN 1987*a*).

A one-month study on the time-related variability of the organic acid content in freshly-collected silver and downy birch sap, carried out by the same authors, revealed similar changeability for three studied trees. Seasonal changes, in this case, affected the organoleptic properties of tree sap and its quality for production of bottled birch sap. The organic acid content, responsible for the taste valued by consumers, grew in time and ranged from about 0.2 to about 0.6 g dm⁻³ of malic acid, from about 0.1 to about 0.2 g dm⁻³

of succinic acid and from about 0.01 to about 0.04 g dm⁻³ of citric acid in silver birch tree sap (KALLIO, AHTONEN 1987b).

Similar differences were detected by AHTONEN and KALLIO (1989), who studied the amino acids content in tree sap of three silver birch trees and three downy birch trees. The amino acids content in sap determines the intensity of Maillard reaction which occurs in a birch syrup production process. Within one month, differences ranged from 0.1 to 2.0 mg dm⁻³ in the alanine content, from 0.2 to 1.4 mg dm⁻³ in leucine, from 0.4 to 3.8 mg dm⁻³ in proline, from 10.3 to 188 mg dm⁻³ in glutamine and from 32.7 to 163 mg dm⁻³ in citrulline (AHTONEN, KALLIO 1989).

The time-related variability of the mineral content in birch tree sap obtained in our study can be also analysed in the nutritional context. Reference of the high changeability of the mineral content (Figures 15-19) to the Polish

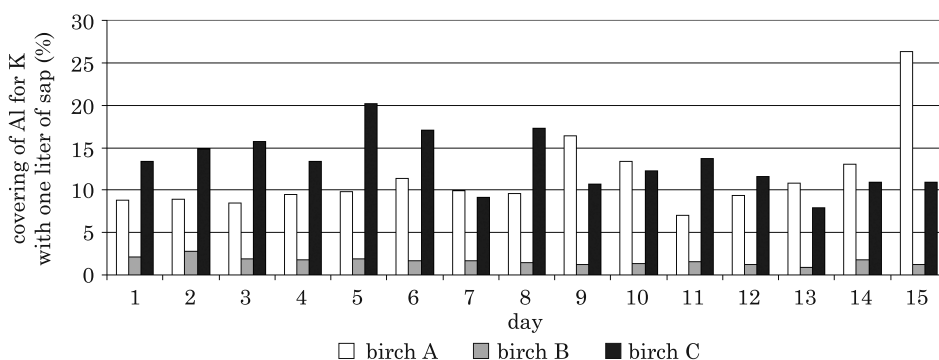


Fig. 15. Covering the adequate intake for potassium with one liter of sap

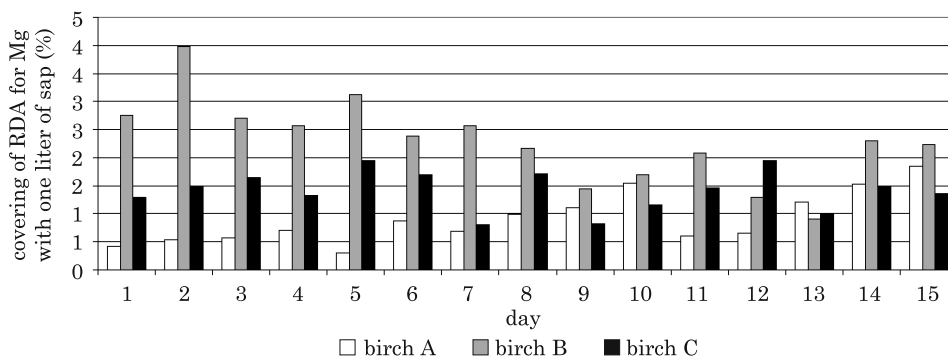


Fig. 16. Covering the recommended dietary allowance for magnesium with one liter of sap

nutritional standards (JAROSZ 2012) translates directly into nutritional benefits of drinking one liter of birch sap a day. For potassium, the adequate intake value offered by one liter of sap collected during two weeks is as follows: 8.49 to 26.34% for tree A, from 0.9 to 2.80% for tree B and from 9.17 to 20.23% for tree C (Figure 15). For zinc (Figure 18), the RDA standard is

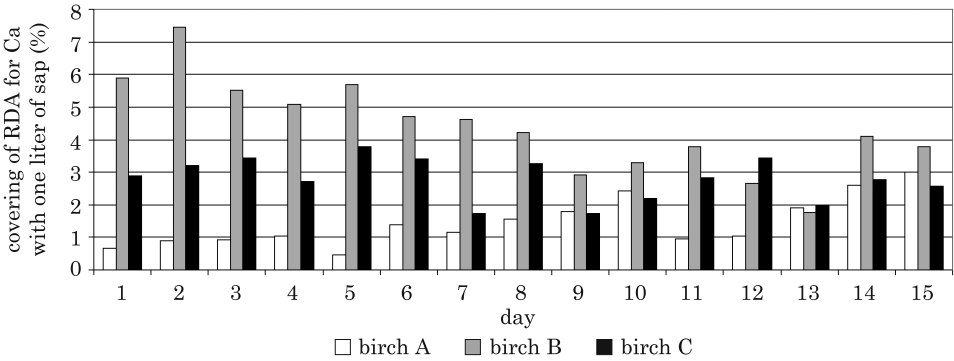


Fig. 17. Covering the recommended dietary allowance for calcium with one liter of sap

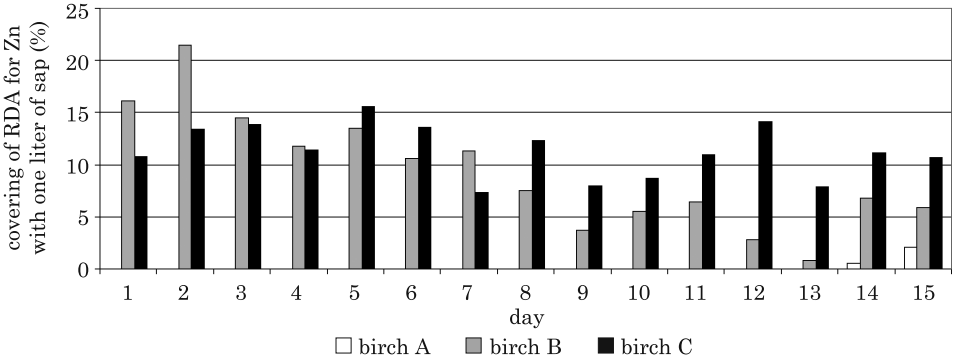


Fig. 18. Covering the recommended dietary allowance for zinc with one liter of sap

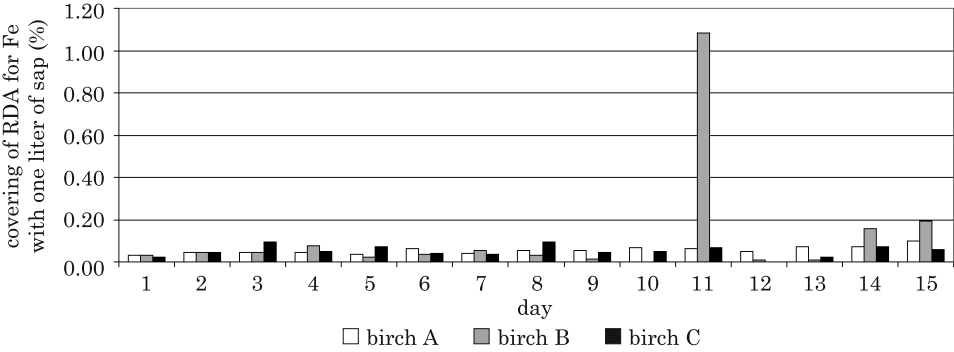


Fig. 19. Covering the recommended dietary allowance for iron with one liter of sap

covered from 0 to 2.11% for tree A, from 0.85 to 21.50% for tree B and from 7.34 to 15.63% for tree C. For iron, only for one of the studied trees and only on a single day, the RDA standard was covered by above 1% (Figure 19).

This study of the time-related variability in the tree sap mineral composition suggests more than just very high differences for the consecutive days

of measurements. Based on the results, it can be stated that there is no point in time when birch sap invariably achieves better nutritive values. This is proven by the fact that birch trees B and C had a higher content of minerals at the beginning of sap collection, while tree A produced sap richest in minerals at the end of the experiment. Moreover, it is impossible to assess the nutritional value of tree saps, understood as the mineral content, from the physical parameters of birch saps. The values of the examined parameters did not correspond in a satisfactory way to the mineral content. Nonetheless, electrolytic conductivity may reflect more faithfully the nutritional benefits. The higher its value is in the saps from two out of three birch trees, the higher the expected concentration of minerals important for humans, i.e. calcium, zinc and potassium.

The described variability in the mineral composition of birch saps shows that much caution is necessary when analysing the results for a single date of collection, as is the case for most results presented in the reference works (VIŠKELIS, RUBINSKIENE 2011, KŪKA et al. 2013, BILEK et al. 2015a, BILEK ET AL. 2016a). The current study revealed that the assessment of the mineral composition of tree sap should be carried out with at least several collections in a sap collection period as a single collection promotes unreliable, selective results. The current results also indicate that such monitoring tests should be carried out for a single tree and should not be based on the time-related variability obtained by several collection instances from several trees, as was done for example by JEONG-JEONG et al. (2012), who evaluated the seasonal variability of birch sap mineral composition but used a different tree for every collection date. The results provided by JEONG-JEONG et al. (2012) indeed indicate differences between the collected sap batches but they are much smaller than the ones demonstrated in the presented study (Table 4, Figures 7-13). It is worth noticing that the results presented in this paper, such as the mineral content in birch saps collected for two weeks, by excluding the risk of chance results due to a single collection, has helped to detect a one-off, significant increase in the concentration of all the minerals studied.

CONCLUSIONS

1. Differences in the mineral composition of tree saps over a two-week study period raise doubt about nutritional benefits of their content.
2. Examination of the mineral composition of tree sap should be based on several samplings from a single tree, as a single collection may produce results deviating from the usual values.
3. Based on the results, it can be concluded that there is no point in time when birch sap invariably achieves superior nutritive values.

REFERENCES

- AHTONEN S., KALIO H. 1989. *Identification and seasonal variations of amino acids in birch sap used for syrup production*. Food Chem., 33: 125-132. DOI: 10.1016/0308-8146(89)90115-5
- BILEK M., STAWARCZYK K., ŁUCZAJ Ł., CIEŚLIK E. 2015A. *Content of selected minerals and inorganic anions in tree saps from Podkarpace region*. ŻNTJ/Food.Science.Technology.Quality, 3(100): 138-147 DOI: 10.15193/zntj/2015/100/046. (in Polish)
- BILEK M., STAWARCZYK K., GOSTKOWSKI M., OLSZEWSKI M., KĘDZIORA K.M., CIEŚLIK E. 2016. *Mineral content of tree sap from the Subcarpathian region*. J. Elem., 21(3): 669-679. DOI: 10.5601/jelem.2015.20.4.932
- CHOI Y. H., HAN S. S., LEE H. O., BAEK S. H. 2005. *Biological activity of bioactive components from Acer ginnala Max*. Bull. Korean Chem. Soc., 26(9): 1450-1452.
- ESSIAMAH S. 1980. *Spring sap of trees*. Ber. Deut. Bot. Ges., 93: 257-267.
- HARJU L., HULDÉN S.-G. 1990. *Birch sap as a tool for biogeochemical prospecting*. J Geochem. Explor., 37(3): 351-365.
- HOLGATE K.C. 1950. *Changes in the composition of maple sap during the tapping season*. <http://ecommons.library.cornell.edu/bitstream/1813/4305/1/bulletin742.pdf>.
- JAROSZ M. (ed.) 2012. *Nutritional standards for the Polish population. Amendment*. IŻŻ, Warszawa. (in Polish)
- JEONG J.S. LEE C.H., KIM H.Y., HWANG I.G., SHIN C.S., PARK E.S., LEE J., JEONG H.-S. 2011. *Characteristic of Goroshoe (Acer mono Max.) sap with different collection times after ultra filtration*. J. Korean Soc. Food Sci. Nutr., 40(5): 753-758. DOI: 10.3746/jkfn.2011.40.5.753
- JEONG S.J., LEE C.H., KIM H.Y., LEE S.H., HWANG I.G., SHIN C.S., LEE J., JEONG H.S. 2012. *Quality characteristics of the white birch sap with varying collection periods*. J. Korean Soc. Food Sci. Nutr., 41(1): 143-148. DOI: 10.3746/jkfn.2012.41.1.143
- KALIO H., AHTONEN S. 1987A. *Seasonal variations of the acids in birch sap*. Food Chem., 25: 285-292. DOI: 10.1016/0308-8146(87)90015-X
- KALIO H., AHTONEN S. 1987B. *Seasonal variations of the sugars in birch sap*. Food Chem., 25: 293-304. DOI: 10.1016/0308-8146(87)90016-1
- KŪKA M., ČAKSTE I., GERŠEBEKA E. 2013. *Determination of bioactive compounds and mineral substances in Latvian birch and maple saps*. Proc. Latv. Acad. Sci. Sect. B Nat. Exact Appl. Sci., 67(4-5): 437-441. DOI: 10.2478/prolas-2013-0069
- LAROCHELLE F., FORGET E., RAINVILLE A., BOUSQUET J. 1998. *Sources of temporal variation in sap sugar content in a mature sugar maple (Acer saccharum) plantation*. Forest Ecol. Manag., 106: 307-313.
- LEE C.-H., CHO Y.-M., PARK E.-S., SHIN C.-S., LEE J.-Y., JEONG H. S. 2009. *In vivo immune activity of sap of the white birch (Betula platyphylla var. japonica)*. Korean J. Food Sci. Technol., 41(4): 413-416.
- MOON H.-S., KWON S.-D., PARK S.-B., GOO J.-W. 2004. *Sap collection and major components of Acer mono in Mt. Jiri*. Korean J. Ecol., 27(5): 263-267. DOI: 10.5141/JEFB.2004.27.5.263
- PAPP N., CZÉGÉNYI D., HEGEDŰS A., MORSCHHAUSER T., QUAVE C. L., CIANFAGLIONE K., PIERONI A. 2014. *The uses of Betula pendula Roth among Hungarian Csángós and Székelys in Transylvania, Romania*. Acta Soc. Bot. Pol., 83(2): 113-122. DOI: 10.5586/asbp.2014.011
- PEEV C., DEHELEAN C., MOGOSANU C., FEFLEA F., CORINA T. 2010. *Spring drugs of Betula pendula Roth.: Biologic and pharmacognostic evaluation*. Stud. Univ. VG, SSV, 3: 41-43.
- QADIR S. A., KIM C. H., KWON M. C., LEE H. J., KANG H. Y., CHOI D. H., LEE H. Y. 2007. *Comparison of Anticancer and Immuno-Modulatory Activities in the different parts of the Acer mono Max. and Acer okamotoanum*. Korean J. Med. Crop Sci., 15(6): 405-410.
- RASTOGI S., PANDEY M. M., RAWAT A. K. S. 2015. *Medical plants of the genus Betula – traditional uses and a phytochemical-pharmacological review*. J. Ethnopharmacol., 159: 62-83. DOI: 10.1016/j.jep.2014.11.010

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- SVANBERG I., SÖUKAND R., ŁUCZAJ Ł., KALLE R., ZYRYANOVA O., DÉNES A., PAPP N., NEDELICHEVA A., ŠEŠKAUSKAITĖ D., KOŁODZIEJSKA-DEGÓRSKA I., KOŁOSOVA V. 2012. *Uses of tree saps in northern and eastern parts of Europe*. Acta Soc. Bot. Pol., 81(4): 343-357. DOI: 10.5586/asbp.2012.036
- VIŠKELIS P., RUBINSKIENĖ M. 2011. *The chemical composition of birch sap*. Sodininkystė ir Daržininkystė, 30(3-4): 75-81. (in Lithuanian)
- YOON S.L., JO J.S., KIM T.O. 1992. *Utilization and tapping of the sap from birches and maples*. Mokchaekonghak., 20(4): 15-20.