

Bioaccumulation of Macro- and Microelements in Herbaceous Plants in the River Valley

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ABSTRACT

The research was done in the upper course of the Kamienna Creek which is the left-bank tributary of River Słupia situated in the northern part of Poland within Leśny Dwór Forest Inspectorate area. The aim of the study was the comparison of accumulation properties of herbaceous plants in spring niches in relation to macro- and microelements. The shoots of research plant species showed a good supply of macro- and micronutrients. The highest contents of nutrients were found in the shoots of *Athyrium filix-femina* (Ni), *Caltha palustris* (Mg, Ca, Sr), *Cardamine amara* (K, Zn, Fe, Al), *Carex rostrata* (Mn) and *Solanum dulcamara* (N, P, Cu), and the lowest in shoots of *Ajuga reptans* (P, Zn, Mn), *Cardamine amara* (N, Cu) and *Carex rostrata* (K, Mg, Ca, Sr, Ni, Fe, Al). Herbaceous plants accumulated from 1767.23 mmol·kg⁻¹ (*Carex rostrata*) to 2739.87 mmol·kg⁻¹ (*Caltha palustris*) of all the analyzed elements. Macronutrients dominated in all herbaceous plant species (>99%), and microelements ranged from 0.33% in *Solanum dulcamara* to 0.67% in shoots *Cardamine amara*. The share of nitrogen was from 38.8% to 56.8% of this amount, phosphorus from 2.9% to 3.9%, potassium from 28.5% to 40.6%, magnesium from 4.8% to 7.6%, and calcium from 4.6% to 16.4%. A large share of iron (from 33.7% *Athyrium filix-femina* to 39.5% *Caltha palustris*), manganese (from 9.2% *Cardamine amara* to 28.8% *Carex rostrata*) and aluminum (from 16.7% *Carex rostrata* to 40.8% *Cardamine amara*) in total measured components indicates excessive downloading them through plants. During the three years of research done in spring niches, it was found that some plant species take up nutrients in the quantities exceeding their physiological demand, which enables to use some of them for forming e.g. artificial wetlands, stopping many impurities and forming protective barriers.

Keywords: riparian forest, peatbogs, herbaceous plants, nutrients, accumulation

INTRODUCTION

The effectiveness of nutrient uptake by plants is largely determined by the factors dependent on them, such as species, age, developmental phase, availability of components in soil and ionic interactions of synergistic and antagonistic nature [Ostrowska and Porębska 2002, Veselkin, et al. 2014]. The amount of components taken up is conditioned by the physiological demand for macro- and micronutrients [Kabata-Pendias and Pendias 1999], but it can also occur in the passive way due to the environmental pollution [Parzych 2016]. The nutrients taken up are used to build tissues and participate in many

metabolic transformations. Seasonal variability of the environment and varied requirements of plants during the growing season determine the dynamic nature of the plant-environment relationship, especially in headwater ecosystems, where underground waters flowing to the surface create specific conditions for the development of soils [Karlsson et al. 2005, Jonczak and Parzych 2016, Jonczak et al. 2016] and plants [Parzych and Jonczak 2018]. A permanent excess of water creates favourable conditions for the accumulation of organic matter and development of dome-shaped bogs, typical for the headwater areas. Paludification of the area is conducive to the development of the rich diversity of

plant species [Décamps et al. 2004, Osadowski 2006, Pielech et al. 2015]. The studies carried out so far indicate that some species of plants occurring within the mid-forest headwater niches have a high capacity for accumulation of macro- and micronutrients [Maine et al. 2006, Hazlett et al. 2008, Parzych et al. 2017, Parzych and Jonczak 2018]. The retention of nutrients in shoots of herbaceous plants is one of the most important processes occurring in river valleys, which act as buffer zones [Tufekcioglu et al. 2003, Hefting et al. 2005, Raty et al. 2010]. Species diversity and accumulation properties of herbaceous plants are the subject of numerous studies due to the significant impact of vegetation on the physicochemical properties of waters [Małek et al. 2010, Parzych et al. 2016, 2017]. The comparison of accumulation properties involving selected plant species in relation to macro- and microelements in the areas unaffected by anthropogenic factors, will allow to broaden the current knowledge about the possibility of using some of them, e.g. in water treatment processes [Viers et al. 2012, Parzych 2016].

The aim of the work was to compare the accumulation properties of *Ajuga reptans*, *Athyrium filix-femina*, *Caltha palustris*, *Cardamine amara*, *Carex rostrata* and *Solanum dulcamara* growing over dome bogs in the mid-forest headwater niches in the river valley, in relation to macro- and micronutrients.

MATERIAL AND METHODS

Stand characteristic

The research was carried out in northern Poland, in the forest inspectorate of Leśny Dwór (54°19'N, 17°10'E), in the upper course of the Kamienna Creek, left-bank tributary of the Słupia River (Fig. 1). The headwater niche chosen for research is located in a hilly upland cut with numerous streams, developed from boulder clays and fluvio-glacial sands. The area of the Kamienna Creek basin is covered by forests characterized by spatially diversified species composition, with the dominance of beech, pine and spruce within upland and black alder in the valley bottom [Parzych et al. 2017]. Sampling points were located in the riparian headwater forest with the black alder stand (*Alnus glutinosa*). The forest stand overgrows bogs cut with headwater streams, built of alder peat with interbeddings of alder-sedge peat [Jonczak et al. 2015a].

Soil and plant sampling

In the headwater riparian forest, there were two research sites located in the central part of the selected dome peat bogs. The soil samples were collected from the following layers: 0–10, 10–20 and 20–30 cm, due to the largest cluster of roots. Within each site, representative species of herbaceous plants, characterized by the highest frequency and density, were selected: *Ajuga reptans* L. (*Aju_rep*), *Athyrium filix-femina* L. Roth (*Ath_fil*), *Caltha palustris* L. (*Cal_pal*), *Cardamine amara* L. (*Car_ama*) from site 1 and *Carex rostrata* Stokes (*Car_ros*) and *Solanum dulcamara* L. (*Sol_dul*) from site 2 (Table 1). The nomenclature of plants growing on bogs was given according to Mirek et al. [2002]. The plant samples were collected for testing in May, July and September in 2012–2014. A single sample consisted of aerial shoots originating from a dozen or so specimens of a given species. In total, 54 plant samples were collected for the study.

Soil and plant analysis

After being transported to the laboratory, the soil samples were dried at 65°C, and milled into powder. The plants were rinsed in distilled water to remove residual soil, then dried at 65°C and homogenised in a laboratory mill (IKA A11). Prior to the analyses, the samples were stored in tightly sealed polyethylene bags. Both in soil and plant samples, nitrogen was determined using the Kjedahl method (Büchi K-350), and phosphorus with spectrophotometric method involving ammonium molybdate (UV-VIS, Hitachi U-5100) after digestion of samples in a mixture of 98% H₂SO₄ and 30% H₂O₂. For the determination of K, Mg, Ca, Zn, Cu, Ni, Mn, Fe, Al and Sr, the samples were digested in a mixture of 65% HNO₃ and 30% H₂O₂ and then deionized water (Hydrolab HLP10) was added to the volume of 50 ml. The contents of K, Mg, Ca, Zn, Cu, Ni, Mn and Fe were determined with atomic absorption spectrometry using the AAnalyst 300 apparatus (Perkin Elmer), and Al and Sr by means of microwave plasma atomic emission spectrometry (Agilent 4100, MP-AES). The apparatus was calibrated based on Merck standard solutions (1 g/1000 mL). All analyzes were performed in triplicate.

Data analysis

The distribution of data on the physicochemical properties of soils and the chemical composition of plants was tested using Shapiro Wilk test.

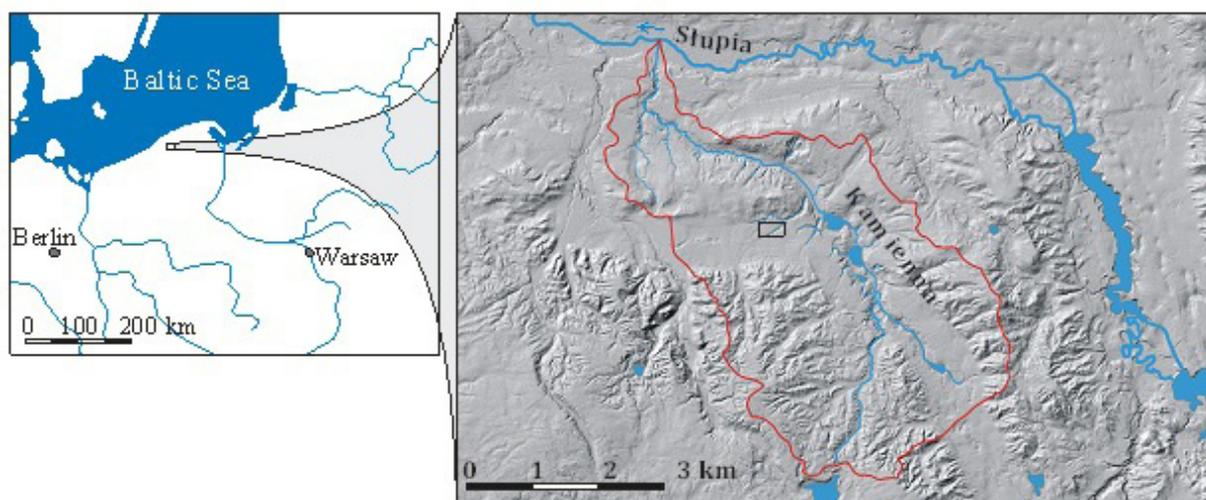


Figure 1. Hydrographic network, the boundaries of the catchment area of the Kamienna river and research area on the background of airborne LIDAR based Digital Elevation Model (DEM)

The results were presented in tables and figures, compared using non-parametric U Mann Whitney and Kruskal-Wallis tests. *Statistica 7.1* software was used to develop the results. The demand of the studied plant species for nutrients was described using the ANE method (*Accumulation Nutrient Elements*), [Ostrowska and Porębska 2002]. The sum of components (Y) in $\text{mmol} \cdot \text{kg}^{-1}$ was calculated based on a formula:

$$Y = \sum (Z : z) \quad (1)$$

where: Z – content of the element in $\text{mg} \cdot \text{kg}^{-1}$
 z – atomic weight/ion valency

After the calculation of Y , the percentage (X) of each element in the sum of:

$$X = [(Z : z) \cdot 100] \cdot Y^{-1}$$

was calculated.

The studied plant species were grouped due to the similarity in the percentage of macro- and microelements in the sum of the accumulated components by means of the cluster method (Ward method).

RESULTS AND DISCUSSION

Physicochemical properties of soil

Due to the statistically insignificant differences in the physicochemical properties of soil samples between 0–10, 10–20 and 20–30 cm layers – in the further part of the work, reference is made to the mean values for the 0–30 cm layer. Within the studied headwater niche, there were

peat soils with diversified thickness, not exceeding 1 m. The content of organic matter remained on average at 21.9% (site 1) and 32.2% (site 2) (Table 1) it and slightly changed with depth. These soils were characterized by weakly acidic pH, relatively poor nitrogen, potassium and magnesium content and on average, rich in phosphorus and calcium. The content of micronutrients in the analyzed soil layers was low and characteristic for peat soils not burdened with the influence of anthropogenic factors [Jonczak et al. 2014]. The solubility of most chemical compounds is small in terms of neutral and alkaline reactions [Smal and Salomons 1995], and increases with the lowering of the pH values [Gworek 2006]. Nitrogen compounds show the highest bioavailability at pH 6.0–8.0, phosphorus at pH 6.5–8.0, potassium at pH 6.0–10.0, and calcium, magnesium and strontium at pH 6.5–8.5. The increase in zinc mobility occurs most effectively at pH 6.0, manganese at pH 6.0 and 8.0, copper and nickel at pH 5.5, iron at pH 4.0, and aluminum at pH 5.5 and below [Kabata-Pendias and Pendias 1999].

Statistically significant differences in active acidity (pH, H_2O) and in the concentration of potassium in the soil in the 0–30 cm layer between the sites were shown (Table 1). The soils in the studied headwater niche exhibited a number of specific features, resulting from their functioning in the spring water area, as a transition zone between the underground and surface part of the water cycle in river basins [Jonczak 2011]. Permanent flow of groundwater above the mineral substrate towards the river occurs in these soils, resulting in characteristic vertical gradients of

Table 1. Physicochemical properties of soils (mean \pm SD) in 0–30 cm layer in the river valley with results of U Mann Whitney test

Parameter	Location 1	Location 2	U Mann Whitney test ($p < 0.05$)
OM, %	21.9 \pm 1.5	32.3 \pm 11.0	-
pH (H ₂ O)	*6.1 \pm 0.1	*5.7 \pm 0.2	0.049
pH (KCl)	*5.4 \pm 0.1	*5.3 \pm 0.1	-
N	9143.1 \pm 822	11021.0 \pm 4072	-
P	6947.2 \pm 1033	6283.6 \pm 2326	-
K	663.1 \pm 10	1785.9 \pm 806	0.049
Mg	898.4 \pm 19	2082.9 \pm 1086	-
Ca	7641.3 \pm 409	10524.7 \pm 3996	-
Sr	44.5 \pm 2	57.8 \pm 24	-
Zn	40.7 \pm 8	62.0 \pm 26	-
Cu	7.3 \pm 0.9	10.8 \pm 4.6	-
Ni	6.7 \pm 0.7	9.4 \pm 4.8	-
Fe	6221.5 \pm 629	13198.9 \pm 6859	-
Mn	244.2 \pm 65	348.2 \pm 149	-
Al	4928.9 \pm 209	7901.9 \pm 4216	-

* – median, p – significance level, – no significant differences

concentrations of various components [Jonczak et al. 2015a]. The macro and micronutrients released in the processes of organic matter decomposition [Jonczak et al. 2015b] were easily washed away by the flowing spring waters beyond the reach of the plant root system [Parzych et al. 2017].

Macro- and microelements concentrations in plants

The content of macro- and microelements in the studied plants varied depending on the species. The highest concentrations of nitrogen and phosphorus were found in the shoots of *Solanum dulcamara* (20 830 mg·kg⁻¹ and 3 483 mg·kg⁻¹ respectively), and the lowest in the case of *Cardamine amara* (14 030 mg·kg⁻¹) and *Ajuga reptans* (2 019 mg·kg⁻¹), respectively (Fig. 2). According to Ostrowska and Porębska [2002], the natural content of nitrogen in green parts of plants is usually in the range from 13 000 to 31 000 mg·kg⁻¹ and phosphorus from 1 000 to 4 000 mg·kg⁻¹. In riparian forests, vegetation usually shows a good supply of biogens due to the high level of water table and easier access to many nutrients, in comparison to other forest ecosystem [Jansson et al. 2007, Kuglerová et al. 2014]. According to Krzywy [2007] the strong humidity of the soil, characteristic of spring areas, has a positive effect on the uptake of phosphorus by plants.

The highest concentration of potassium was demonstrated in the shoots of *Cardamine amara* (41 123 mg·kg⁻¹), and the lowest in the case of

Carex rostrata (19 648 mg·kg⁻¹), (Fig. 1). For all species concerned, the results obtained exceeded the natural K content in plants (2000–18000 mg·kg⁻¹) [Ostrowska and Porębska 2002]. Potassium is often absorbed by plants in excess [Krzywy 2007], especially in the forest ecosystems with a high level of groundwater table [Parzych et al. 2017]. High K content in the shoots of various plant species found in heavily moistened areas has been confirmed in the literature [Samecka-Cymerman and Kempers 2007, Horska-Schwarz and Spałek 2008, Parzych et al. 2017].

The most biogen-rich species was *Caltha palustris*, which accumulated the highest amounts of Mg (5016 mg·kg⁻¹), Ca (17 197 mg·kg⁻¹) and Sr (152.3 mg·kg⁻¹), (Fig. 2, 3). Simultaneously, Mg (2017 mg·kg⁻¹), Ca (4247 mg·kg⁻¹) and Sr (35.9 mg·kg⁻¹) were found in the shoots (Fig. 2, 3). According to Ostrowska and Porębska [2002] the optimal content of magnesium and calcium in the shoots of most plant species is in the range: 1000–3000 mg·kg⁻¹ (Mg) and 1000–33 000 mg·kg⁻¹ (Ca). Comparable Mg contents (2000 mg·kg⁻¹) and significantly lower Ca concentrations (2500 mg·kg⁻¹) in surface shoots of *Carex rostrata* were shown by Czerwiński and Prac [1995].

The shoots of the analyzed plants showed a good supply of micronutrients. Among the species studied, the highest amounts of Ni were found in *Athyrium filix-femina*, Zn, Fe and Al in *Cardamine amara*, Mn in *Carex rostrata*, and Cu in *Solanum dulcamara*. The smallest concentrations of Zn, Mn occurred in the shoots of *Ajuga*

reptans, Cu in *Cardamine amara*, and Sr, Ni, Fe and Al in *Carex rostrata*. All of the analyzed species showed increased concentrations of nickel (>10 mg/kg) [Kabata-Pendias and Pendias 1999], (Fig. 3). The main source of nickel in the studied headwater riparian forest is organic precipitation and soil. The research results obtained by Jonczak et al. [2014] and Jonczak and Parzych [2014] indicate that the main fraction of organic fall (alder leaves) contains much higher Ni concentrations than soil. This element is released very quickly during the mineralization processes and supplies spring waters, from where it is taken up by plants [Jonczak et al. 2015b]. The Kruskal-Wallis test showed statistically significant differences in the concentration of Ca and Sr at $p < 0.001$, K and Mg at $p < 0.01$ as well as P, Mn and Al at $p < 0.05$ between the tested plant species (Fig. 2, 3).

The amount of nutrients taken in by plants depends to a large extent on the demand for individual components and on soil properties [Kabata-Pendias and Pendias 1999], (Tab. 1). The reaction of soils in the studied niche promoted the uptake of macronutrients and limited the availability of some micronutrients for plants.

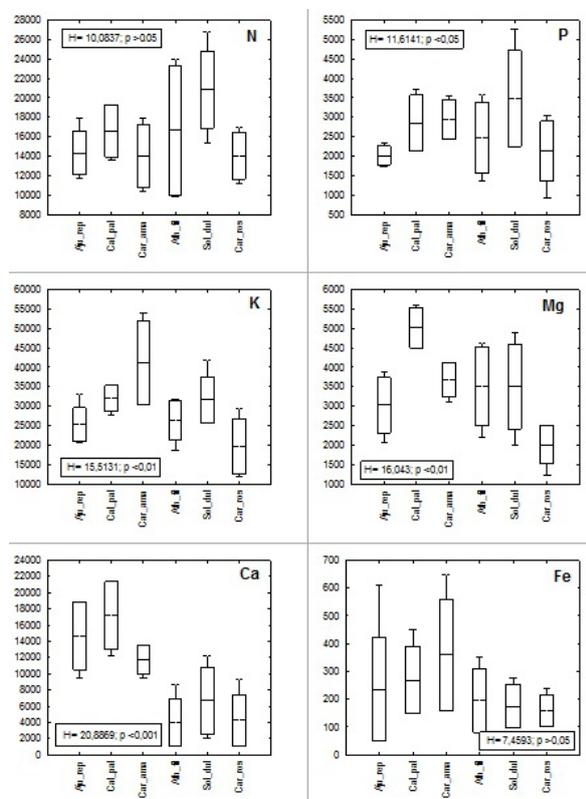


Figure 2. Average contents ($\text{mg}\cdot\text{kg}^{-1}$) N, P, K, Mg, Ca and Fe in shoots of herbaceous plants with the results of Kruskal-Wallis test. Rectangle – standard deviation, mustache – min-max

Macro- and microelements accumulation in plants

On the basis of the concentration of elements in plants, the sum of macro- and microelements was calculated using the ANE method (*Accumulation Nutrient Elements*), according to Ostrowska and Porębska [2002]. The sum of ingredients reflects the so-called nutritional factor. The value of the sum of ingredients and its ionic composition determine the flow of nutrients between the soil and the plant. The percentage share of individual components in their sum depends on the nutritional requirements of plants in relation to the analyzed nutrients [Parzych and Cymer 2014].

The shoots of herbaceous plants of the headwater niche tested accumulated from 1767.23 $\text{mmol}\cdot\text{kg}^{-1}$ (*Carex rostrata*) to 2739.87 $\text{mmol}\cdot\text{kg}^{-1}$ (*Caltha palustris*) of all analyzed components (Table 2). Macronutrients, the share of which was over 99%, were dominant in all analyzed species, and micronutrients constituted from 0.33% in *Solanum dulcamara* to 0.67% in *Cardamine amara* shoots. The ionic composition of the sum of macroelements in the shoots of the headwater plants

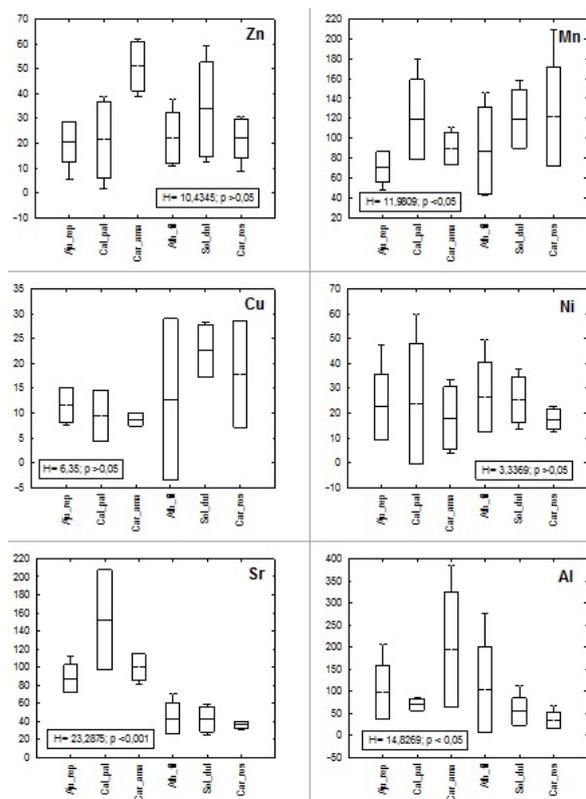


Figure 3. Average contents ($\text{mg}\cdot\text{kg}^{-1}$) Mn, Cu, Ni, Zn, Sr and Al in shoots of herbaceous plants with results of Kruskal-Wallis test. Rectangle – standard deviation, mustache – min-max

Table 2. Average accumulation of macro- and microelements in shoots of plants in the river valley

Species	Σ macro, mmol _c ·kg ⁻¹	Σ micro, mmol _c ·kg ⁻¹ (participation %)	Σ macro + Σ micro mmol _c ·kg ⁻¹
<i>Ajuga reptans</i>	2230.62	11.00 (0.49)	2241.61
<i>Athyrium filix-femina</i>	2191.52	10.41 (0.49)	2201.92
<i>Caltha palustris</i>	2739.87	12.20 (0.44)	2752.07
<i>Cardamine amara</i>	2597.65	17.61 (0.67)	2615.26
<i>Carex rostrata</i>	1767.23	7.67 (0.43)	1774.90
<i>Solanum dulcamara</i>	2724.10	9.09 (0.33)	2733.20
Range	1767.23 – 2739.87	7.67 – 17.61	1774.90 – 2733.20

was significantly different, depending on the species, compared to plants growing on the soils with much moisture content [Ostrowska and Porębska 2002, Parzych 2015].

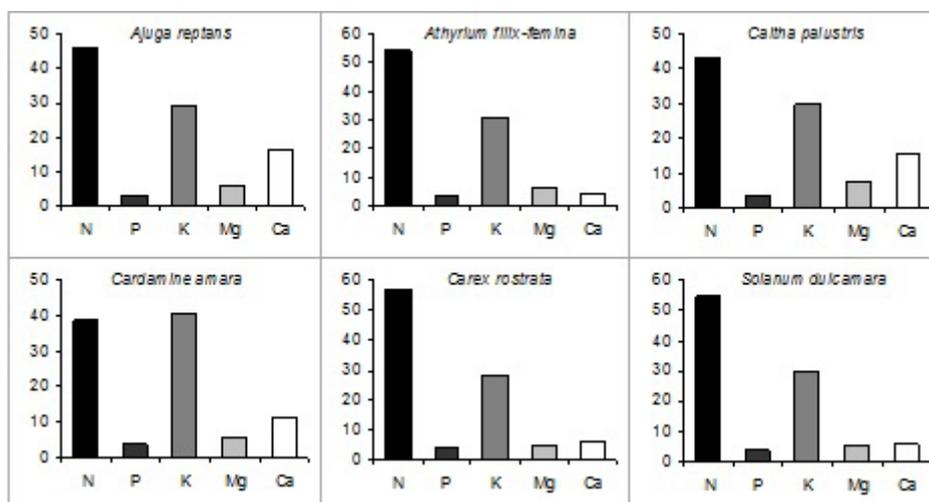
The obtained sums of macro- and micronutrients for plants in the studied spring niche were comparable for the majority of species growing in the riparian forests [Parzych et al. 2018] and much higher than in the case of other species found in river valleys [Parzych et al. 2015]. The share of nitrogen constituted from 38.8% (*Cardamine amara*) to 56.8% (*Carex rostrata*) of this sum, phosphorus from 2.9% (*Ajuga reptans*) to 3.9% (*Carex rostrata*), potassium from 28.5% (*Carex rostrata*) to 40.6% (*Cardamine amara*), magnesium from 4.8% (*Carex rostrata*) to 7.6% (*Caltha palustris*), and calcium from 4.6% (*Athyrium filix-femina*) to 16.4% (*Ajuga reptans*), (Fig. 4). The high proportion of iron (from 33.7% *Athyrium filix-femina* to 39.5% *Caltha palustris*), manganese (from 9.2% *Cardamine amara* to 28.8% *Carex rostrata*) and aluminum (from 16.7% *Carex rostrata* to 40.8% *Cardamine amara*) in the total of the measured components (Fig. 5) indicates their excessive absorp-

tion by plants from soil, which was favoured by a slightly acidic reaction (Table 1).

Among the species examined, similarities were observed regarding the percentage of macro- and microelements in the shoots of herbaceous plants (Fig. 6). Both *Solanum dulcamara* and *Carex rostrata* were characterized by a very similar percentage of all tested components. *Cardamine amara* and *Athyrium filix-femina* exhibited a similar proportion of P, Mg and Zn, and *Caltha palustris* and *Ajuga reptans* of K, Ca, Zn, Ni and Fe in total amount of the analyzed nutrients.

CONCLUSION

The herbaceous plants in the studied head-water niche showed a good supply of both macro and micronutrients. The highest amounts of nutrients were found in the shoots of: *Athyrium filix-femina* (Ni), *Caltha palustris* (Mg, Ca, Sr), *Cardamine amara* (K, Zn, Fe, Al), *Carex rostrata* (Mn) and *Solanum dulcamara* (N, P, Cu). The lowest concentrations of the nutrients were found in the shoots of *Ajuga reptans* (P, Zn, Mn),

**Figure 4.** Percentage share of N, P, K, Mg and Ca in amount macronutrients in herbaceous plants

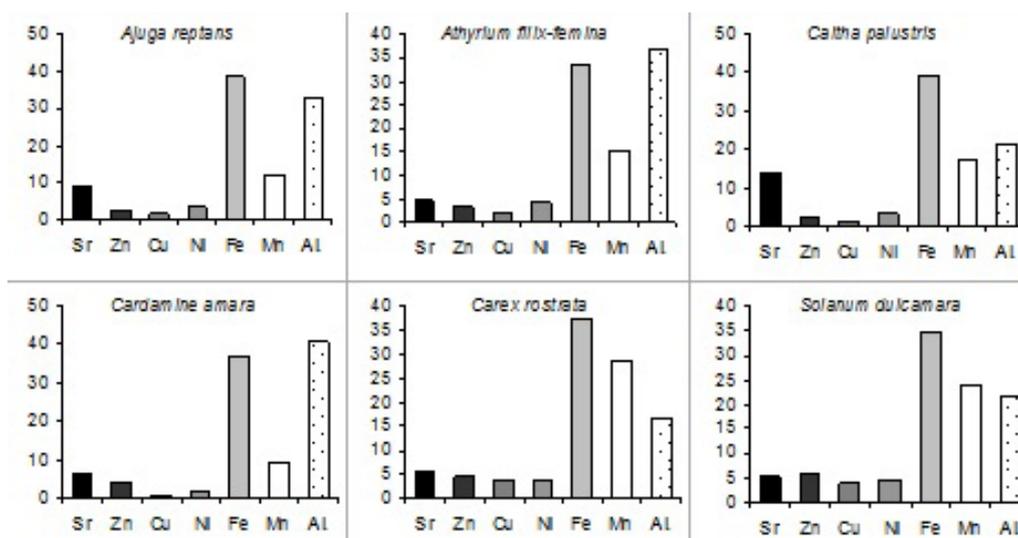


Figure 5. Percentage share of Fe, Zn, Mn, Cu, Ni, Sr and Al in amount micronutrients in herbaceous plants

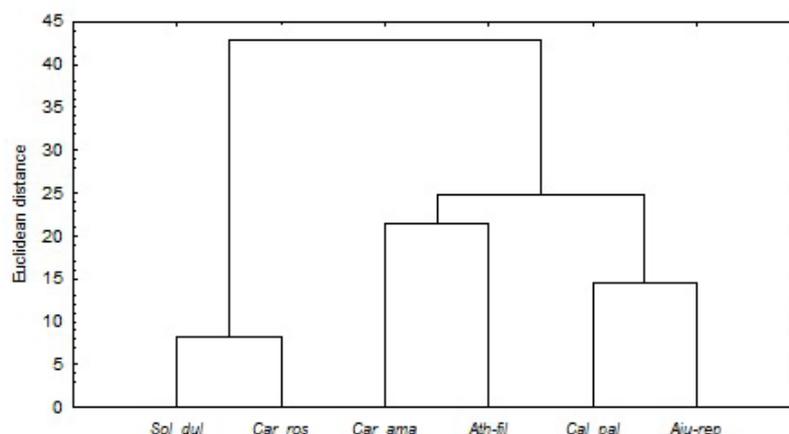


Figure 6. Dendrogram of hierarchical cluster analysis of percentage of macro- and micronutrients in shoots of herbaceous plants (Ward's method)

Cardamine amara (N, Cu) and *Carex rostrata* (K, Mg, Ca, Sr, Ni, Fe, Al).

The shoots of herbaceous plants accumulated from 1767.23 mmol_c:kg⁻¹ to 2739.87 mmol_c:kg⁻¹ of all analyzed components. Macronutrients, the share of which was over 99%, were dominant in all analyzed species, and micronutrients constituted from 0.33% to 0.67%. The share of nitrogen constituted from 38.8% to 56.8% of this sum, phosphorus from 2.9% to 3.9%, potassium from 28.5% to 40.6%, magnesium from 4.8% to 7.6%, and calcium from 4.6% to 16.4%. The high proportion of iron (33.7–39.5%), manganese (9.2–28.8%) and aluminum (16.7–40.8%) in total of the measured microcomponents indicates their excessive absorption by plants. Among the studied herbaceous plants, *Solanum dulcamara* and *Caltha palustris* accumulated the largest amounts

of nutrients. The presence of these species in river valleys strengthens the effectiveness of the protective barrier constituted by herbaceous vegetation.

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