Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2020.25462

186 (2020) 350–360
May

The influence of plants on water quality in stream flowing through of mid-forest spring niche

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Received 23 September 2019; Accepted 15 January 2020

ABSTRACT

In this paper, we evaluated the effects of herbaceous plants and bryophytes on the physicochemical properties of waters flowing through the mid-forest spring niche. The research was carried out in the Kamienna River valley, in Northern Poland. In streams, submerged macrophytes belonging to the *Pellio endiviifoliae-Cratoneuretum commutati* community were found. Herbaceous plants (*Cardamine amara, Glyceria plicata, Mentha aquatica, Stellaria uliginosa*) and bryophytes (*Brachythecium rivulare, Palustriella commutata, Pellia endiviifolia*) of the highest classes of stability and with the highest cover coefficients were chosen for chemical research. During growing seasons, the pH and concentrations of potassium (K^+), nitrate (NO_3^-), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), iron (Fe^{3+}) and manganese (Mn^{2+}) ions in the stream flowing through the mid-forest spring niche were significantly modified by plants via the uptake and accumulation of macro- and trace elements *C. amara* had the greatest capacity to modify stream ion concentrations among the plants assessed. The plant stood out against other species with its above-average capacity to accumulate phosphorus (P), potassium (K) and magnesium (Mg). This species accumulated high quantities of nutrients (3,439.7 mmol × kg^{-1}), which were mainly comprised of macroelements. On the other hand, in *P. endiviifolia* thalli, above-average levels of Fe and Mn were noted. The accumulation potentials of *C. amara* and *P. endiviifolia* indicate that the presence of these species significantly affect the physicochemical properties of water. This information has an important practical dimension, which is related to the potential use of *C. amara* and *P. endiviifolia* as water quality modifying agents.

Keywords: Stream; Bryophytes; Herbaceous plants; Accumulation nutrients elements; Hierarchical cluster analysis; Water purification

1. Introduction

The greatest degree of plant species diversity is found in river valleys [1–4]. Further, diverse plant species play an essential role in shaping the physicochemical properties of flowing waters [5,6]. The species composition of plant communities occurring in the zone of river water flow depends mainly on water and soil conditions [4,7–9]. The direction and range of changes in the physicochemical parameters of waters are determined primarily by the species composition of plant communities, soil fertility, and anthropogenic factors [10–13].

Macrophytes growing along streams and rivers and their valley bottoms, in addition to the stabilization of the shoreline, accumulate high levels of nutrients, often in quantities exceeding physiological demands, which affect physicochemical properties of flowing waters [14]. Studies on the accumulation potential of plants are important for identifying new practices that can be used to improve water quality.

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Presented at the 14th Conference on Microcontaminants in Human Environment, 4–6 September 2019, Czestochowa, Poland

Data previously reported in the literature have indicated the high level of potential of plants growing in river valleys to selectively accumulate above-average quantities of nutrients [15–17]. Studies on the accumulation potential of macrophytes in river valleys [18–22] confirm that plants depending on the species take up to 47% of nitrogen compounds and about 60% of phosphorus compounds from flowing waters, and are protected against eutrophication. The quantity of the elements accumulated by plants depends to a large extent on factors dependent on the plants themselves (species, age, developmental phase), as well as the bioavailability of nutrients [23]. The diverse requirements of plants and the seasonal variability of the environment make the nature of the plant-environment relationship in the growing season very dynamic [24–26]. Despite extensive information available in the literature regarding the relationship between the physicochemical properties of waters and the content of macro- and trace elements in plants, the accumulation potential of many species remains undetermined. This applies especially to headwater areas [27] since they are ecological niches containing high levels of biological diversity [28]. Moreover, the physicochemical transformation of waters in the upper part of the stream network is often neglected, despite its significant impact on the water quality of lower courses [25,29]. The characterization of the capacity of macrophytes to accumulate nutrients in streams and their impact on the physicochemical properties of waters flowing through the mid-forest spring niche may provide researchers with the information needed to use particular species in water treatment processes [17,30,31]. Indication of species which, under conditions of limited anthropopressure, are good accumulators of selected elements, may significantly affect efforts to improve water quality [32].

This study aimed to determine whether the presence of submerged macrophytes in streams affected the physicochemical properties of waters by accumulating nutrients. For this purpose, (1) a species inventory of macrophytes present in the stream was performed, (2) the plant chemistry was assessed three times throughout growing seasons from 2012 to 2014, and (3) the physicochemical properties of stream water immediately in front of and behind the spring niche were determined throughout monthly cycles (2012–2014). The conducted research allowed researchers to compare the quality of stream waters in spring niche in different growing seasons and beyond. Further, we were able to establish which physicochemical parameters studied were significantly modified by the vegetation of the spring niche and plant species with the highest accumulation potential concerning the nutrients tested.

2. Materials and methods

2.1. Study area

The research was carried out in the upper course of the Kamienna Creek, a left-bank tributary of the Słupia River, in Northern Poland (54°19′N; 17°10′E), Fig. 1. The catchment of the creek studied was located in post-glacial landscape of Central Pomerania. It was entirely covered by forests of diverse spatial composition, which contained a predominance of beech, pine and spruce in its upland portion and black alder in its valley bottom [26]. The area is influenced by anthropogenic factors that have the potential to modify the eco-chemical state, and overall quality, of the ecosystem. Soils surrounding the spring niche (Sapric Histosols) were characterized by their spatially diverse thickness that did not exceed 1 m and their acidity. The soil contained high concentrations of nitrogen, potassium, calcium, and magnesium, and had relatively low levels of phosphorus [12]. Underground water systems that flow along the valley slopes form a network of small streams that cross the peatland, which is covered with herbaceous vegetation and bryophytes. The highest degree of plant species diversity of was found in the immediate vicinity of groundwater outflow. Most species developed on the sandy bottom of the stream, except for bryophytes, which sporadically covered stones and dead branches.

2.2. Sampling and analysis of water

Water samples were collected for testing every month, from January 2012 to December 2014, immediately in front of and behind the spring niche. A total of 72 water samples were analyzed throughout the 36-month study. Water temperature; pH, using the potentiometric method (CPI 551 Elmetron, Poland); electrolytic conductivity (EC) (CC 315, Elmetron, Poland) and dissolved oxygen content (O_2), using an oxygen probe (HI 9146), were measured in the field. Other parameters were measured in the laboratory. For this purpose, water samples were collected in 500 mL polyethylene bottles. Bicarbonate (HCO_3^-) ion content was determined by titration with 0.1 mol × L^{-1} hydrochloric acid (HCl) solution, while K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-} concentrations were assessed using ion chromatography (881 Compact IC pro, Metrohm, Switzerland). Further, Zn^{2+}, Fe^{3+}, Cu^{2+}, Ni^{2+}, and Mn^{2+} concentrations were assessed using atomic absorption spectrometry (Analyst 300, Perkin-Elmer (USA)), and Al^{3+} and Sr^{2+} concentrations were determined by microwave plasma atomic emission spectrometry (Agilent 4100 MP-AES, Australia). Water samples were filtered through a 0.20 μm sterile syringe filter and diluted with deionized water at a ratio of 1:4. The accuracy of the output was assessed using a certified reference material (Multi-element Ion Chromatography Standard, Certified 89 866-50ML-F, Fluka, France). Thanks to the autosampler system, all analyzes of examined water samples were performed within 24 h of the moment they were sampled.

2.3. Sampling and analysis of plants

Within the spring niche, a plant inventory was made using the Braun–Blanquet method [33], consisting of 12 phytosociological images. Individuals of particular taxa were identified and counted, and then they were classified in the appropriate phytosociological system [34]. The constancy classes of species (S) and coverage factors (D) [35] in the years 2012–2014 were characterized. The nomenclature of herbaceous plants is given according to Mirek et al. [36] and bryophytes according to Ochyra et al. [37].

Seven representative species with the greatest constancy classes and coverage coefficients were selected for chemical analysis. These consisted of herbaceous plants including *C. amara* L., *G. plicata* (Fr.) Fr., *M. aquatica* L., and *S. uliginosa*

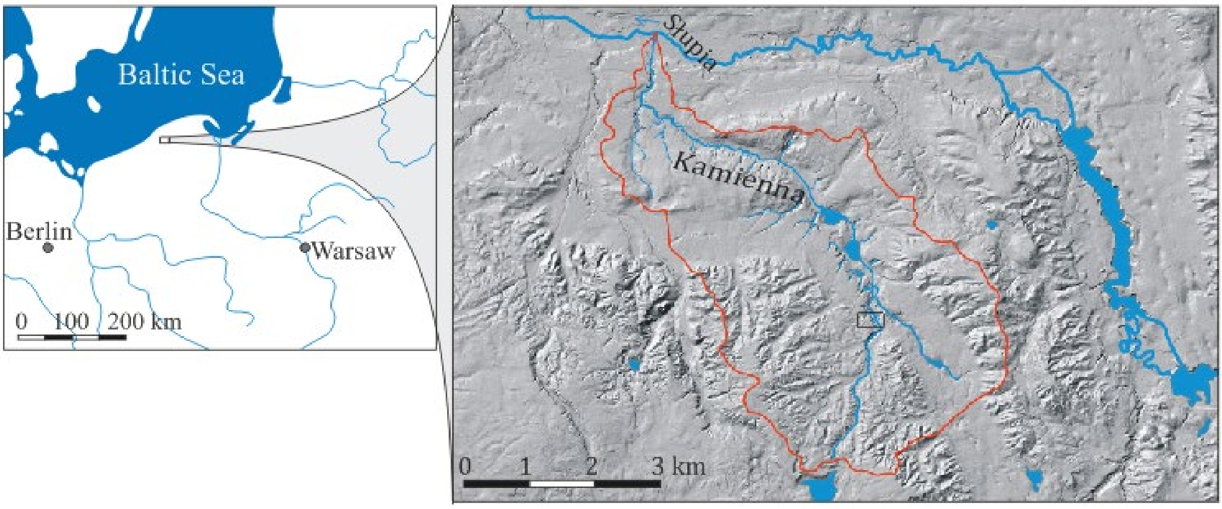

Fig. 1. Hydrographic network (in blue), the boundaries of the Kamienna Creek catchment (in red) and research spring niche location (in black).

Murray and bryophytes: *B. rivulare* Schimp, *P. commutata* (Hedw.) Ochyra and *P. endiviifolia* (Dickson 1801) Dumortier 1835. Plant samples were collected three times during each growing season (May, July, September) between 2012 and 2014. A single sample consisted of shoots from a dozen or so specimens of a given species. In the case of herbaceous plants, parts of aboveground shoots were collected and in the case of bryophytes, the entire thalli were collected. Sixty-three plant samples were collected in total for chemical analysis. In the laboratory, the plants were washed using distilled water to remove residual sediments, then dried (65°C) in drying oven and homogenized (IKA A11). Until the analysis, samples were stored in closed polyethylene bags. Nitrogen was determined using the Kjeldahl method (automatic distiller, K-360 Büchi, Switzerland) after samples were digested in a mixture of 98% H_2SO_4 and 30% H_2O_2 in a 1:1 ratio by volume. P, K, Ca, Mg, Zn, Fe, Cu, Ni, Mn, Al, and Sr were analyzed after samples were digested in a mixture of 65% HNO_3 and 30% H_2O_2 at a 1:1 ratio by volume and subsequently supplemented with deionized water (Hydrolab HLP10, Poland) to a volume of 50 mL. The content of P in solutions was determined by the molybdenum-blue method (spectrophotometer UV-VIS, Hitachi U-5100, Japan), whereas K, Mg, Ca, Zn, Cu, Ni, Fe, and Mn content was determined by flame atomic absorption spectrometry using an Analyst 300 spectrometer from Perkin-Elmer (USA). Al and Sr content were determined in the same solutions by atomic microwave plasma atomic emission spectrometry (Agilent 4100 MP-AES , Australia). All the analysis were performed in three replicates. The tests were carried out using the original standards provided by Merck (Germany) (1 g$\cdot$1 L^{-1}). The quality of analysis was controlled based on certified reference material (aquatic plants, CRM 060 , Belgium). The error associated with the analysis of certified materials did not exceed the range deemed permissible (±3%).

2.4. Statistical analysis

The distribution of data regarding the physicochemical properties of water samples and the macro- and trace-element content within plants were tested using the Shapiro–Wilk test. Physicochemical characteristics of the water flowing in and out of the spring niche were compared using the non-parametric Mann–Whitney U test. The results of assessments of stream water were interpreted within growing seasons (May, June, July, August, September) and out of growing seasons (January, February, March, April, October, November, December) from 2012 to 2014. In order to characterize the submerged macrophytes in the stream, constancy classes (S) and coverage factors (D) for each species were determined. Constancy classes determined the relative species purity within a syntax on. Five classes were defined as follows: Class I (1%–20% of occurrences), II (21%–40%), III (41%–60%), IV (61%–80%) and class V (81%–100%) [34]. Coverage factor (D) numerically expresses the average share of particular species and was calculated from Eq. (1) as follows:

$$D = \frac{\left(\text{sum of the average coverage percentage} \times 100\right)}{\text{number of phytosociological images}} \quad (1)$$

Both constancy classes and coverage factors determine the role of a particular species in the community which makes it possible to compare individual species. Data assessing macro- and trace element content in bryophytes and herbaceous plants were compared using the Kruskal–Wallis test (K–W) and the post hoc (Tukey HSD) test. The accumulation of macro- and trace elements in the species studied were calculated using the accumulation nutrient elements method, which comprehensively reflects so-called nutritional factors [38]. The value of the sum of components and its ionic composition determine the flow of elements between the soil and the plant. The percentage of each component in the sum depends on the nutritional requirements of the plant species about macro- and trace elements [38,39]. The sum of elements (Y) in mmol$_c$ kg^{-1} was calculated based on Eq. (2):

$$Y = \Sigma\left(\frac{Z}{z}\right) \quad (2)$$

where Z indicates the concentration of each element (mg × kg^{-1}) and z indicates atomic weight divided by ion valence. After the calculation of Y, the percentage (X) of each element in the sum was calculated based on Eq. (3) as follows:

$$X = \left[\left(\frac{Z}{z} \right) \times 100 \right] \times Y^{-1} \tag{3}$$

Diversity in terms of the varied accumulation potential of tested plants in relation to macro- and trace element content is presented on a Ward method dendrogram. This method illustrates the hierarchical structure of a set of objects due to the decreasing similarity between them [40]. The Ward method differs from all others because it uses the analysis of variance approach to estimate the distance between clusters. It is treated as very effective, although it tends to create small size clusters. All calculations were performed using the software package Statistica 13.3. (Statsoft Inc., USA).

3. Results

3.1. Physicochemical properties of waters in stream

Water temperatures recorded during the 36-month study period were between 6.3°C and 9.5°C and were closely related to weather conditions. The water samples were either neutral or slightly alkaline, and pH values ranged from 7.40 to 7.61. The average EC of water flowing into the niche was between 292.86 and 364.40 µS × cm^{-1} and decreased as water flowed through the niche, reaching values that ranged from 283.57 to 345.00 µS × cm^{-1}. The concentration of dissolved oxygen varied spatially, from 5.77 to 5.88 mg × L^{-1} and 8.49 to 8.60 mg × L^{-1} in front of and behind the spring niche, respectively (Table 1).

Further, Na^+ content was determined to be between 5.19 and 5.36 mg × L^{-1} in front of the spring niche and 5.18 and 5.22 mg × L^{-1} behind the niche (Table 1). Slightly lower concentrations of K^+ ions were determined, in which values ranged from 1.03 to 1.24 mg × L^{-1}. Values determined depended on the position and date of sampling. Samples had very low concentrations of NH_4^+ ions (0.06–0.19 mg × L^{-1}) throughout the research period. Cations were predominantly identified as Ca^{2+}, which were present at concentrations between 42.20 and 59.25 mg × L^{-1}. Other cations, including Mg^{2+} (2.70–3.77 mg × L^{-1}), Fe^{3+} (1.14–1.46 mg × L^{-1}) and Mn^{2+} (0.12–0.30 mg × L^{-1}), were present at significantly lower concentrations. Further, Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, and Sr^{2+} concentrations were below the limit of detection (<0.01 mg × L^{-1}) irrespective of the location sampled and time point of collection (Table 3).

The most commonly identified anion was HCO_3^-, which was present at concentrations between 163.83 and

Table 1
Mean values of physicochemical parameters of water inflowing and outflowing from the mid-forest spring niches over the growing seasons and during growing seasons with U Mann–Whitney test results

Parameter	Outside the growing seasons			Growing seasons		
	Inflow of water	Outflow of water	U Mann–Whitney test (p-values)	Inflow of water	Outflow of water	U Mann–Whitney test (p-values)
Temperature (°C)	7.3 ± 1.08	6.3 ± 2.03	–	8.6 ± 0.42	9.5 ± 0.79	–
pH	7.40 ± 0.20	7.58 ± 0.26	–	7.45 ± 0.26	7.61 ± 0.22	<0.05
EC (µS cm^{-1})	292.86 ± 71.45	283.57 ± 67.52	–	364.40 ± 86.62	345.00 ± 85.35	–
O_2 (mg L^{-1})	5.77 ± 1.04	8.60 ± 1.28	<0.01	5.88 ± 0.56	8.49 ± 0.40	<0.01
Na^+ (mg L^{-1})	5.36 ± 0.51	5.18 ± 0.47	–	5.19 ± 0.36	5.22 ± 0.38	–
K^+ (mg L^{-1})	1.24 ± 0.22	1.15 ± 0.25	–	1.16 ± 0.11	1.03 ± 0.12	<0.05
NH_4^+ (mg L^{-1})	0.17 ± 0.16	0.19 ± 0.14	–	0.06 ± 0.11	0.11 ± 0.21	–
Mg^{2+} (mg L^{-1})	3.12 ± 1.32	2.70 ± 1.40	–	3.77 ± 1.85	3.57 ± 1.96	–
Ca^{2+} (mg L^{-1})	45.10 ± 20.25	42.20 ± 17.82	–	59.25 ± 12.88	58.03 ± 15.11	–
HCO_3^- (mg L^{-1})	181.80 ± 4.24	163.83 ± 6.52	<0.01	182.38 ± 6.95	164.08 ± 3.33	<0.01
Cl^- (mg L^{-1})	7.34 ± 0.76	7.56 ± 0.90	–	6.68 ± 1.05	6.44 ± 1.00	–
NO_3^- (mg L^{-1})	2.28 ± 1.18	1.23 ± 0.89	–	2.57 ± 0.95	0.91 ± 0.46	<0.05
SO_4^{2-} (mg L^{-1})	21.54 ± 2.49	22.45 ± 1.94	–	20.14 ± 1.11	21.32 ± 0.56	<0.05
PO_4^{3-} (mg L^{-1})	0.80 ± 0.16	0.52 ± 0.39	–	0.93 ± 0.14	0.45 ± 0.46	<0.05
Zn^{2+} (mg L^{-1})	<0.01	<0.01	–	<0.01	<0.01	–
Fe^{3+} (mg L^{-1})	1.46 ± 0.3	1.43 ± 0.4	–	1.45 ± 0.3	1.14 ± 0.2	<0.05
Cu^{2+} (mg L^{-1})	<0.01	<0.01	–	<0.01	<0.01	–
Ni^{2+} (mg L^{-1})	<0.01	<0.01	–	<0.01	<0.01	–
Mn^{2+} (mg L^{-1})	0.29 ± 0.07	0.28 ± 0.05	–	0.30 ± 0.04	0.12 ± 0.02	<0.05
Al^{3+} (mg L^{-1})	<0.01	<0.01	–	<0.01	<0.01	–
Sr^{2+} (mg L^{-1})	<0.01	<0.01	–	<0.01	<0.01	–

182.38 mg × L–1, depending on the sampling point (Table 1). Concentrations of NO_3^- ranged from 2.28 to 2.57 mg L^{-1} in front of the niche and from 0.91 to 1.23 mg L^{-1} behind the spring niche, and showed seasonal variation. The average SO_4^{2-} content of water samples ranged from 20.14 to 21.54 mg L^{-1} in front of the spring niche and from 21.32 to 22.45 mg L^{-1} directly behind the niche (Table 1). The concentration of PO_4^{3-} ions in front of the niche ranged from 0.80 to 0.93 mg L^{-1} and decreased as a result of contact with macrophytes. In such instances, concentrations ranged from 0.45 to 0.52 mg L^{-1}.

3.2. Characteristics of plant communities in stream

The spring niche studied contained macrophytes belonging to the *Pellio endiviifoliae-Cratoneuretum commutati* community and those that associated with *Cratoneurion commutati*, 34 species, including 25 vascular plants and 9 bryophytes were identified. Among these plants, *C. amara*, *Cratoneuron filicinum*, *Chrysosplenium alternifolium*, *Geranium robertianum*, *Lemna minor*, *Veronica beccabunga*, *P. endiviifolia*, *B. rivulare*, *P. commutata*, *Epilobium parviflorum* and *Oxalis acetosella* were identified. The number of species in individual phytosociological images ranged from 8 to 15 (average 12). Coverage of the bottom of the stream by bryophytes ranged from 45% to 95% (average 75%), while coverage by herbaceous plants ranged from 20% to 60%, (average 40%). The species chosen for chemical tests belonged to the highest constancy class and had the greatest coverage factors (Table 2). *P. endiviifolia* and *P. commutata* showed the highest degree of constancy (V), and *Pel_end* had the highest coverage factor (D) among plants assessed. In the group of plants assessed, *B. rivulare* and *Stellaria nemorum* were members of a low constancy class (II) and had the lowest coverage factors (283 and 133, respectively).

Table 2
Characteristic of selected bryophytes (a) and herbaceous plants (b) species

Species	Code	*S*	*D*
Brachythecium rivulare	[a]*Bra_riv*	II	283
Cardamine amara	[b]*Car_ama*	IV	1,475
Glyceria plicata	[b]*Gly_pli*	III	475
Mentha aquatica	[b]*Men_aqu*	IV	767
Palustriella commutata	[a]*Pal_com*	V	729
Pellia endiviifolia	[a]*Pel_end*	V	4,292
Stellaria uliginosa	[b]*Ste_uli*	II	133

Note: *S* – constancy class, *D* – coverage factor

3.3. Macro- and trace elements concentration in plants

The plants selected for subsequent research accumulated elements to varying degrees during the research period. Average nitrogen content values ranged from 9,333.3 mg × kg^{-1} (*Pal_com*) to 25,433.3 mg × kg^{-1} (*Car_ama*) (Fig. 2). The largest variability in N content during growing seasons was found in *Gly_pli*, and the lowest degree of variability was observed in *Pal_com* and *Bra_riv*. Phosphorus content of plants was maintained at the levels from 1,134.0 mg × kg^{-1} (*Pal_com*) to 6,553.6 mg × kg^{-1} (*Car_ama*), and potassium levels ranged from 3,777.9 mg × kg^{-1} (*Pal_com*) to 53,782.2 mg × kg^{-1} (*Car_ama*). Magnesium content ranged from 1,402.7 mg × kg^{-1} (*Bra_riv*) to 4,956.8 mg × kg^{-1} (*Car_ama*), and calcium levels ranged from 5,643.0 mg × kg^{-1} (*Bra_riv*) to 22,153.3 mg × kg^{-1} (*Car_ama*). Further, N/P ratios ranged from 3.87 to 8.23 in bryophytes and 3.88 to 5.11 in herbaceous plants (Table 3). Among the analysed plant species, *Gly_pli* and *Ste_uli* were identified as showing the largest degree of variability with regard to P, K, Mg and Ca content, while

Table 3
Minimum and maximum of macro- and trace elements content (mg kg^{-1}) in bryophytes and herbaceous plants

Elements	Bryophytes		Herbaceous plants		Natural content in plants
	Minimum	Maximum	Minimum	Maximum	
N	9,333.3	14,933.3	14,583.3	25,433.3	13,000–31,000[a]
P	1,134.0	3,854.3	3,192.7	6,553.6	1,000–4,000[a]
K	3,777.9	34,891.1	25,411.1	53,782.2	5,000–12,000[a]
Mg	1,402.7	3,226.0	3,301.2	4,956.8	1,000–4,000[a]
Ca	5,643.0	12,412.2	11,470.4	22,153.3	1,000–33,000[a]
Zn	20.0	46.1	17.1	19.9	10–70[b]
Fe	393.5	3,231.4	219.7	358.1	5–375[b]
Cu	8.3	13.5	10.2	34.7	4–5[b]
Ni	15.9	19.6	9.6	25.9	0.5–5[b]
Mn	180.5	2,866.4	94.3	252.7	10–25[b]
Al	218.9	311.6	72.5	167.5	2–200[b]
Sr	24.0	60.4	35.9	79.6	4.7–50[b]
N/P	3.87	8.23	3.88	5.11	9.5[c]
Fe/Mn	1.13	2.94	1.42	3.46	1.5–2.5[b]

[a][36], [b][38], [c][39]

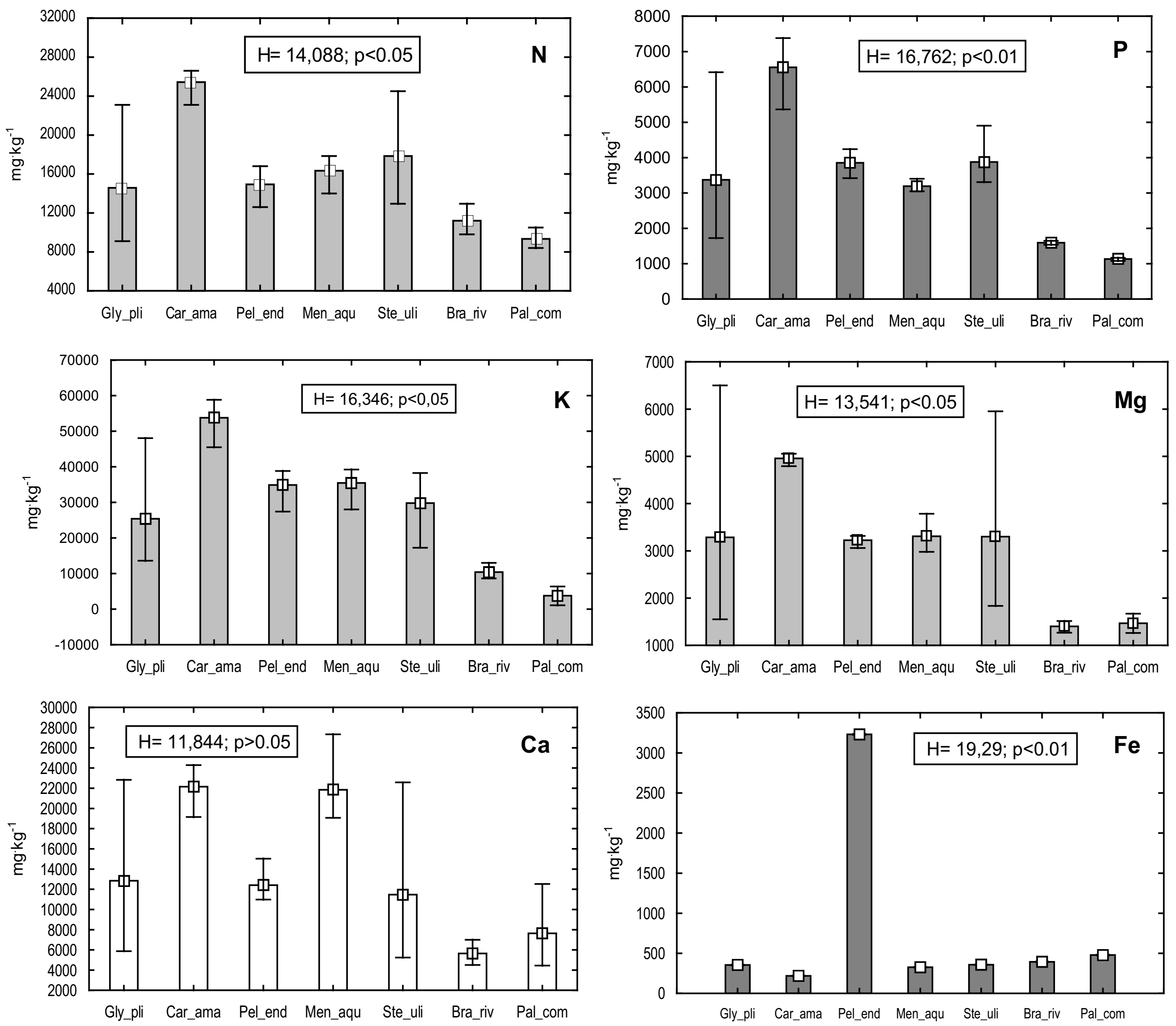

Fig. 2. Mean and range of content of N, P, K, Mg, Ca and Fe in plants in mid-forest spring niches with Kruskal–Wallis (K–W) test results (dark gray – statistically significant at $p < 0.01$, gray – statistically significant at $p < 0.05$, colorless – no statistical significance).

Bra_riv and *Pel_end* showed the smallest degree of variability. In the species considered, very high iron content was found in the thalli of *Pel_end* (3,231.4 mg × kg^{-1}) in comparison with other species including *Car_ama* (217.9 mg × kg^{-1}) and *Pal_com* (479.2 mg × kg^{-1})(Fig. 2).

Levels of zinc in plants assessed ranged from 17.1 mg × kg^{-1} (*Ste_uli*) to 46.1 mg × kg^{-1} (*Pel_end*), copper levels ranged from 8.3 mg × kg^{-1} (*Pal_com*) to 34.7 mg × kg^{-1} (*Car_ama*), and Ni^{2+} levels observed ranged from 9.6 mg × kg^{-1} (*Men_aqu*) to 25.9 mg × kg^{-1} (*Car_ama*) (Fig. 3). Significantly higher levels of manganese, Al^{3+}, and Sr^{2+} were observed, which ranged from 94.3 mg × kg^{-1} (*Car_ama*) to 2,866.4 mg × kg^{-1} (*Pel_end*), 72.5 mg kg^{-1} (*Ste_uli*) to 311.6 mg × kg^{-1} (*Pel_end*) and 24.0 mg kg^{-1} (*Bra_riv*) to 79.6 mg kg^{-1} (*Men_aqu*), respectively. The Fe/Mn ratio varied in both bryophytes and herbaceous plants and ranged from 1.13 to 2.94 and from 1.42 to 3.46, respectively (Table 3).

The results of our studies revealed statistically significant differences with respect to N, K, Mg, and Zn ($p < 0.01$) and P, Fe, Cu, Ni, Mn, Al, and Sr ($p < 0.05$) content between plant species considered (Figs. 2 and 3). The greatest quantities of N, P, K, Mg, Ca, and Ni were found in herbaceous plants (*Car_ama*), and the greatest concentrations of Fe, Zn, Mn, Cu, and Al were found in bryophytes (*Pel_end*), while the greatest concentrations of Sr were found in herbaceous plants (*Men_aqu*) (Table 3). According to results of post hoc Tukey HSD test, differences between *C. amara* and *P. commutata* ($p < 0.001$), *B. rivulare* ($p < 0.01$), *G. plicata* ($p < 0.05$) and *M. aquatica* ($p < 0.05$) (Table 4) were significant.

3.4. Accumulation of macro- and trace elements in plants

Total levels of macro and trace elements present within each species were calculated separately (Table 5). Bryophytes accumulated all elements analyzed at levels ranging from 754.1 mmol$_c$ kg^{-1} (*Pal_com*) to 2,219.6 mmol$_c$ × kg^{-1} (*Pel_end*), and herbaceous plants accumulated levels ranging from 1,836.8 mmol$_c$ × kg^{-1} (*Gly_ply*) to 3,439.7 mmol$_c$ × kg^{-1} (*Car_ama*).

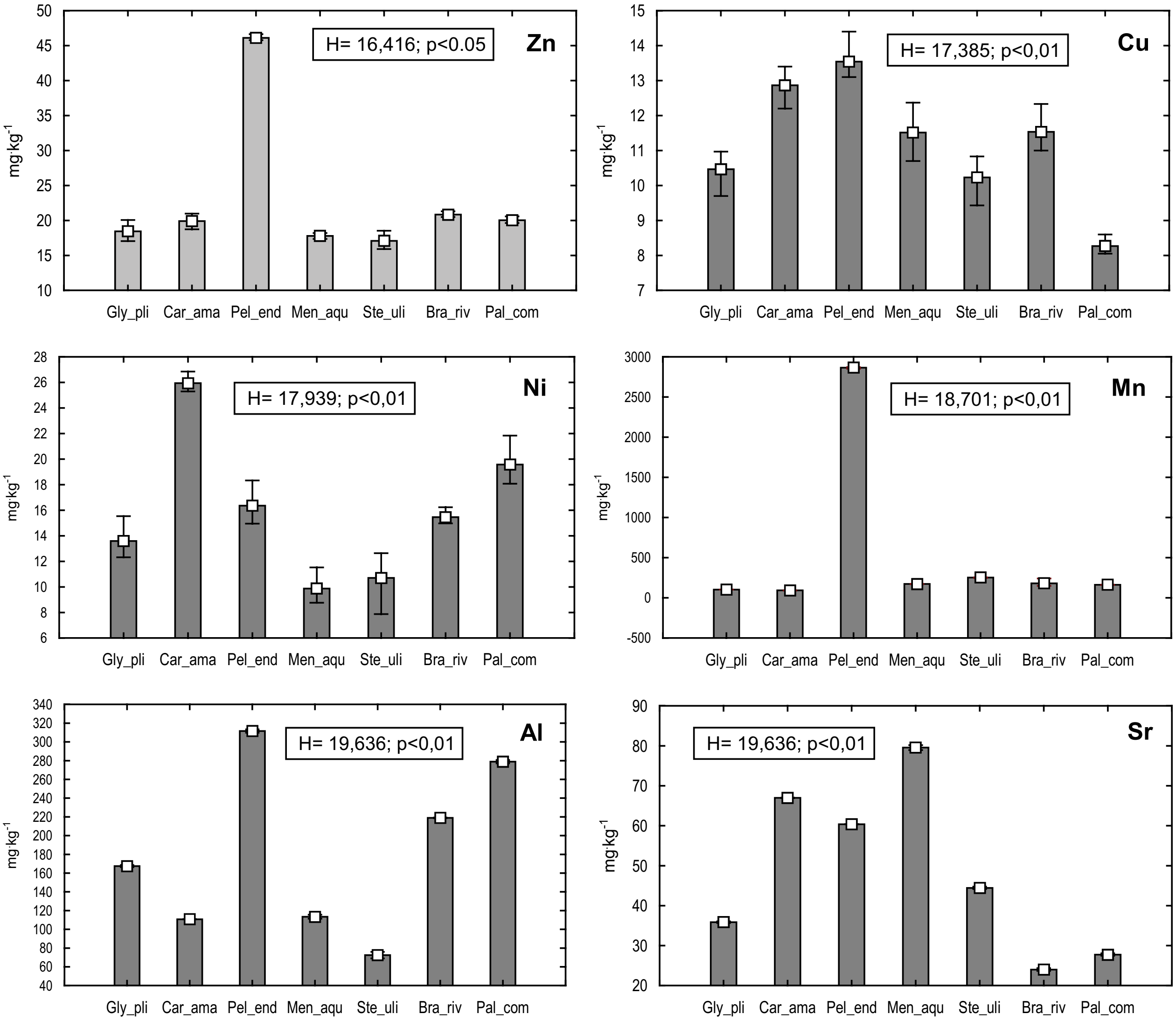

Fig. 3. Mean and range of Zn, Cu, Ni, Mn, Al and Sr content in plants with Kruskal–Wallis (K–W) test results (dark gray – statistically significant at $p < 0.01$, gray – statistically significant at $p < 0.05$, colorless – no statistical significance).

Table 4
Post hoc test results (Tukey HSD test)

Species	*Gly_pli*	*Car_ama*	*Men_aqu*	*Ste_uli*	*Bra_riv*	*Pal_com*	*Pel_end*
Gly_pli		**<0.05**	>0.05	>0.05	>0.05	>0.05	>0.05
Car_ama	**<0.05**		**<0.05**	>0.05	**<0.01**	**<0.001**	>0.05
Men_aqu	>0.05	**<0.05**		>0.05	>0.05	>0.05	>0.05
Ste_uli	>0.05	>0.05	>0.05		>0.05	>0.05	>0.05
Bra_riv	>0.05	**<0.01**	>0.05	>0.05		>0.05	>0.05
Pal_com	>0.05	**<0.001**	>0.05	>0.05	>0.05		>0.05
Pel_end	>0.05	>0.05	>0.05	>0.05	>0.05	>0.05	

Note: bold values are statistically significant

Macroelements made up more than 99% of the total content of the elements assessed in herbaceous plants and ranged from 94.4% to 97.9% of all elements assessed in bryophytes. Macronutrients identified included nitrogen, phosphorus, potassium, magnesium, and calcium, which ranged from 9.7% (*Men_aqu*) to 13.7% (*Car_ama*), 22.4% (*Men_aqu*) to 41.2%

Table 5
Average of macro- and trace elements accumulation (mmol$_c$ kg^{-1}) and mean contribution (%) of elements in the total sum[a] in bryophytes (a) and herbaceous plants (b)

Elements	[a]*Bra_riv*	[b]*Car_ama*	[b]*Gly_pli*	[b]*Men_aqu*	[a]*Pal_com*	[a]*Pel_end*	[b]*Ste_uli*
N	113.9 (12.1%)	468.1 (13.7%)	241.0 (13.2%)	228.1 (9.7%)	81.0 (11.1%)	275.3 (13.1%)	277.0 (13.6%)
P	361.3 (38.4%)	820.4 (23.9%)	470.4 (25.8%)	526.9 (22.4%)	301.1 (41.2%)	481.7 (23.0%)	575.8 (28.2%)
K	267.2 (28.4%)	1,379.0 (40.2%)	651.6 (35.8%)	909.9 (38.7%)	96.9 (13.2%)	894.6 (42.7%)	764.1 (37.4%)
Mg	58.4 (6.2%)	206.5 (6.0%)	137.0 (7.5%)	137.9 (5.9%)	61.2 (8.4%)	134.4 (6.4%)	137.6 (6.7%)
Ca	141.1 (15.0%)	553.8 (16.2%)	321.3 (17.6%)	546.3 (23.3%)	191.0 (26.1%)	310.3 (14.8%)	286.8 (14.0%)
Zn	0.3 (1.6%)	0.3 (2.6%)	0.3 (1.8%)	0.3 (1.9%)	0.3 (1.3%)	0.7 (0.6%)	0.3 (1.8%)
Fe	7.0 (36.1%)	3.9 (33.2%)	6.4 (40.9%)	5.8 (39.7%)	8.6 (37.3%)	57.7 (46.8%)	6.4 (43.2%)
Cu	0.2 (0.9%)	0.5 (4.6%)	0.2 (1.1%)	0.2 (1.2%)	0.1 (0.6%)	0.2 (0.2%)	0.2 (1.1%)
Ni	0.3 (1.4%)	0.4 3.7%)	0.2 (1.6%)	0.2 (1.1%)	0.3 (1.5%)	0.3 (0.2%)	0.2 (1.2%)
Mn	3.3 (16.9%)	1.7 (14.5%)	1.9 (12.0%)	3.1 (21.4%)	3.0 (12.9%)	52.1 (42.3%)	4.6 (31.1%)
Al	8.1 (41.7%)	4.1 (34.8%)	6.2 (39.9%)	4.2 (28.6%)	10.3 (45.0%)	11.5 (9.4%)	2.7 (1.2%)
Sr	0.3 (1.4%)	0.8 (6.5%)	0.4 (2.6%)	0.9 (6.2%)	0.3 (1.4%)	0.7 (0.6%)	0.5 (3.4%)
Σ macro	941.9	3,427.9	1,821.3	2,349.1	731.2	2,096.4	2,041.3
Σ micro	19.5	11.8	15.5	14.7	22.9	123.3	14.8
Σ total	961.4	3,439.7	1,836.8	2,363.8	754.1	2,219.6	2,056.0

[a]Expressed as a form of an amount of these components and their contribution in the total.

(*Pal_com*), 13.2% (*Pal_com*) to 42.7% (*Pel_end*), 5.9% (*Men_aqu*) to 8.4% (*Pal_com*), and 14.0% (*Ste_uli*) to 26.1% (*Pal_com*) of the total quantity of elements assessed. Microelements identified predominantly consisted of iron, which comprised 46.8%, 43.2% and 40.9% of total microelement totals in *Pel_end*, *Ste_uli*, and *Gly_pli*, respectively. Manganese consisted of 42.3% and 31.1%, of microelements in *Pel_end* and *Ste_uli*, respectively, and Al^{3+} made up 45.0%, 41.7%, and 39.9% of the total micronutrient content in *Pal_com*, *Bra_riv* and *Gly_pli* (Table 5). We were able to show that there were statistically significant differences ($p < 0.001$) between the content of trace elements when groups of plants were compared. Data revealed that trace element content ranged from 2.03% to 5.56% and 0.34% to 0.84% in bryophytes and herbaceous plants, respectively.

Three groups of plants were identified (Fig. 4) using hierarchical cluster analysis. Group A consisted of both herbaceous plants and bryophytes and included *Gly_pli*, *Pel_end*, *Men_aqu*, and *Ste_uli*. The group was characterized by its high proportion of Fe, Mn and Al (89.7–98.5%) and accumulation of N, P, and K that ranged from 70.8% to 81.9% (Table 5). Group B included *Car_ama*, and accumulated the highest levels of N, P, K, Mg and Ca. Further, the total contribution of Fe, Mn and Al for the group was 82.5%. Group C consisted of bryophytes *Bra_riv* and *Pal_com*. The group had the greatest percentage contribution of Fe, Mn and Al (94.7% and 95.2%, respectively) compared to other studied plants and the average proportion of N, P and K was 78.9% and 65.5%, respectively (Table 5).

4. Discussion

4.1. Physicochemical properties of water

During the research, physicochemical parameter values for waters flowing through the spring niche were significantly variable. Over the growing seasons, these differences were related to the oxygen saturation levels of the water and the reduced solubility of carbon dioxide. Outflowing groundwater was oxygen-poor. However, during the flow through the spring niche, water was increasingly oxidized [6,41], and CO_2 was depleted. This process was more profoundly observed in the growing seasons, since flowing water in these periods had greater temperatures and, therefore, the solubility of CO_2 correspondingly decreased [25]. In addition, in the growing seasons intensive macro- and trace elements uptake by the plants of the *Pellio endiviifoliae-Cratoneuretum commutati*, community-produced the spring waters outflow from leaving the niche with statistically significantly altered ion concentrations (K^+, NO_3^-, PO_4^{3-}, SO_4^{2-}, Fe^{3+}, Mn^{2+}) and pH levels compared to the water that supplied the niche (Table 1). During the period of dynamic growth, plants had an increased demand for nutrients, including K^+, NO_3^- and PO_4^{3-}, Fe^{3+} and Mn^{2+}. This may have led to reductions in their concentrations in headwater streams [9,25,42]. A slightly different situation regarding SO_4^{2-} ion content was observed. Slight increases in SO_4^{2-} ion concentrations in stream waters behind the spring niche, which was likely a result of litterfall decomposition, were much more efficient in the summer period than the outside growing seasons [13]. In the spring studied, in the vicinity of the flowing stream, organic matter accumulates in the form of peat [6,43]. This provides a potential source of ions to the stream. In addition, efficient litterfall decomposition processes enrich spring ecosystems by providing bioavailable nutrients [12].

4.2. Characteristics of plant communities in stream

The submerged macrophytes of the spring niche were classified as members of the *Pellio endiviifoliae-Cratoneuretum commutati* community, which has often been associated with spring waters of Northern Poland [9,44,45]. The

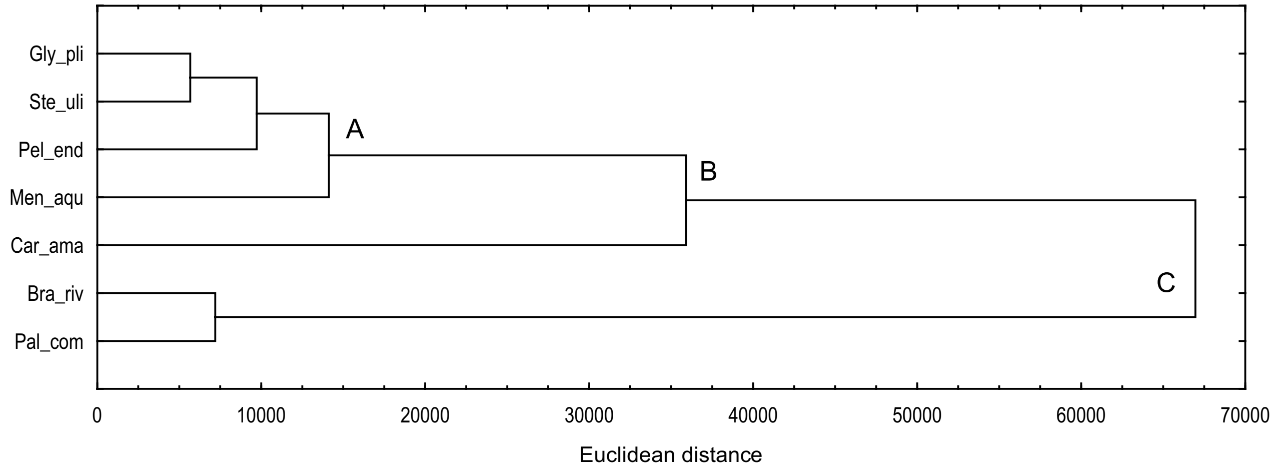

Fig. 4. Similarity of plants species in terms of accumulation potential of macro- and trace elements (Ward's clustering method).

physiognomy of this community was determined by its abundance of *P. endiviifolia* thalli at the bottom of the spring niche, which had a surface area of a few square meters [6]. According to Osadowski [46], this species prefers streams rich in bicarbonates, calcium, and iron, which is typical for water outflowing from deeper aquifers (inter-moraine) [47]. In phytosociological images of this community, researchers observed that it was primarily composed of *P. commutata* (Table 2). *C. amara*, *M. aquatica*, *G. plicata* and *S. uliginosa* were also vascular flora of the community. Bryophytes were represented by *Brachythecium rivulare*, *P. endiviifolia* and *P. commutata* [45]. Species included in this research were characterized by their high constancy class and coverage factors, which allowed researchers to explain the impact of the *Pellio endiviifoliae-Cratoneuretum commutati* community on the quality of water in the stream (Table 1).

4.3. Macro- and trace elements content in plants

The growth and development of macrophytes of the stream had a modifying effect on the physicochemical properties of stream water. The studied plants were generally good suppliers of N, P, Mg, and Ca, and also produced either good or excessive levels of K [48]. Five of the studied species (*Car_ama*, *Ste_uli*, *Men_aqu*, *Pel_end*, *Gly_pli*) accumulated much greater quantities of K than the average physiological demand (2,000–18,000 mg × kg^{-1}) of most plants [39]. Potassium is a macronutrient that plants often accumulate at levels that exceed nutritional needs [45,48,49]. Phosphorus and magnesium content in the majority of the species tested were adequate, except *Car_ama* in which excessive quantities of these macronutrients were found. Among the studied plants, the largest quantities of macroelements were found in *Car_ama* shoots, which differed from other species since it accumulated above-average levels of P, K, and Mg (Table 3). The capacity of the species to accumulate nutrients may be useful for improving physicochemical properties of water with regard to phosphorus, magnesium and potassium levels. The lowest overall content and the smallest degree of dynamics of macronutrients were found in bryophyte species including *B. rivulare* and *P. commutata* (Fig. 2).

Levels of trace elements in-stream macrophytes were relatively low, which was likely a result of the low levels of trace elements present in stream waters (Table 1) and the characteristics of the research site [26]. Among the species studied, *Pel_end* had above-average concentrations of Fe (3,231.4 mg × kg^{-1}) and Mn (2,866.4 mg × kg^{-1}) in its thalli (Fig. 3). Plant tolerance to manganese and iron, however, varies widely. Most plant species contain between 5 and 375 mg × kg^{-1} Fe and 10 to 25 mg × kg^{-1} Mn. For some species, levels of Mn greater than 500 mg × kg^{-1} can be toxic [50,51]. Our research confirmed the strong accumulation potential of *Pel_end* with respect to iron and manganese compounds [6,52]. The capacity of the species to accumulate these elements can be used to facilitate the water treatment processes. The analysis of our data also revealed that increased levels of Ni (>10 mg × kg^{-1}) were observed in *Bra_riv*, *Car_ama*, *Gly_pli*, *Pal_com*, *Pel_end* species and increased levels of Cu (>3 0 mg × kg^{-1}) were observed in *Car_ama* (Table 3).

A comparison of macro- and trace element content (Kruskal–Wallis test) revealed differences between plant species [23]. Further, the post hoc (Tukey HSD) test showed that *Cardamine amara* differed from *P. commutata*, *B. rivulare*, *G. plicata* and *Mentha aquatica* species. According to Ostrowska and Porębska [39,53], plants that accumulate the greatest concentrations of elements have outstanding accumulation properties (Table 3).

4.4. Accumulation of macro- and trace elements in plants

Analyzing the total macro- and trace element values in submerged macrophytes in streams revealed that herbaceous plants accumulated higher average quantities of elements than bryophytes (Table 4). Most plants accumulated between 1,200 and 2,500 mmol$_c$ × kg^{-1} of macro- and microelements in their shoots [39,53]. However, *Car_ama* accumulated a greater levels of (mainly) macroelements (3,439.7 mmol$_c$ × kg^{-1}), indicating that the species has a significant degree of accumulation potential with regard to these elements (Table 4). The percentage of each element of the total was determined primarily by the nutritional requirements of each species considered [38]. Micronutrients make up 1% of the total nutrient content in most plant species [39].

Our results regarding the micronutrient content of herbaceous plants are in accordance with this assertation. However, Bryophytes accumulated micronutrients at levels between 2.0% (*Bra_riv*) to 5.6% (*Pel_end*). When analyzing percentages of trace elements, researches observed that *Pel_end* accumulated above-average quantities of Fe (57.7%) and Mn (52.1%) in comparison to other species (Table 5). An elemental analysis revealed the significant accumulation potential of *Bra_riv* (41.7%) and *Pal_com* (45.0%) for Al^{3+} and *Car_ama* for Ni^{2+} (3.7%). The accumulative potential of an indicated species can be used as a part of treatment efforts to improve water quality.

Both iron and manganese have important physiological functions in plants. Accumulation of manganese is most efficient in either acid (pH < 5.5) or alkaline (pH ~ 8.0) environments. Iron accumulates most efficiently at pH < 5.0. In addition, an excess of Al can accelerate the accumulation of Fe and Mn. In plants, the ratio of Fe to Mn is also very important. Since the studied plants functioned under the same environmental conditions, it was concluded that differences in Fe/Mn values resulted from the varied micronutrient demands of individual species (Table 3). In cases in which Fe/Mn ratios are lower than 1.5, signs of manganese toxicity and iron deficiency in plants can occur, and ratios above 2.5 can also produce harmful symptoms of manganese deficiency [50]. According to Zhiguo et al. [54] maximal plant growth and a maximal supply of macroelements accumulate at an N/P ratio close to 9.5 (Table 3). Submerged macrophytes had much lower N/P ratios than the plants from other areas [55]. This influenced the outflow of mineral forms of nitrogen and phosphorus, keeping it out of the reach of plants growing along the stream [22]. Therefore, it was assumed that the growth and development of plants studied was restricted by the limited bioavailable forms of nitrogen within the reach of their root systems.

5. Conclusions

Our data revealed that submerged macrophytes belonging to the *Pellio endiviifoliae-Cratoneuretum commutati* community had the greatest degree of species diversity and significantly modified the physicochemical properties of stream water by decreasing concentrations of K^+, NO_3^-, PO_4^{3-}, Fe^{3+}, and Mn^{2+} ions. Plant species of the highest constancy class and with the highest coverage factors had (*C. amara*, *P. commutata*, *P. endiviifolia*) had the greatest impact on river quality. In the growing seasons, increased plant demand for nutrients significantly affected water pH in streams flowing through the mid-forest spring niche. Increased concentrations of SO_4^{2-} in waters flowing in the spring niche were a result of the efficient decomposition of organic matter. Among the plants studied, *C. amara* displayed the largest accumulation potential. It accumulated nutrients, mainly macronutrients P, K, and Mg, to higher-than-average levels. The thalli of *P. endiviifolia* also accumulated above-average levels of Fe and Mn microelements. The capacities of *Car_ama* and *Pel_end* to accumulate nutrients suggest that the presence of the species in streams of the mid-forest spring niche is shaped by the physicochemical properties of flowing waters. Similar degrees of variability were not observed outside the growing seasons. This information is practically important since bryophytes and herbaceous plants have the potential to be used to enhance water purification.

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