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Preliminary research of heavy metals content in aquatic plants taken from surface water (Northern Poland)

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ABSTRACT

The examinations of the aquatic plants of the Słupia River were performed in summer 2013 at the research stations situated within the limits of the city of Słupsk. The aim of the research was to evaluate the content of Zn, Fe, Mn, Ni, and Cu in leaves and rhizomes *Glyceria maxima*, *Phragmites australis*, *Typha latifolia*, and *Phalaris arundinacea* and to compare their cumulative properties in the context of selected heavy metals. The content of Zn, Cu, Ni, Mn, and Fe in the sprouts of the aquatic plants showed substantial diversity depending on the species and of sprouts. The tested plants accumulated heavy metals mainly in rhizomes, except for manganese, which, in the case of *P. australis* and *T. latifolia* appeared in larger quantities in the leaves. It was demonstrated that *T. latifolia* mostly cumulated Zn and Ni, and *G. maxima* Mn and Fe. The relationships among the content of the determined heavy metals in the sprouts of macrophytes was identical for all tested species and could be arranged into the following sequences: Mn > Fe > Zn > Ni > Cu in leaves and Fe > Mn > Zn > Ni > Cu in rhizomes. The heavy metals content in the leaves as well as in the rhizomes of the examined macrophytes were substantially correlated with the content of some metals in the bottom deposits of the Słupia River. The non-parametric Mann–Whitney U-test demonstrated a series of statistically vital differences in the content of Zn, Cu, Mn, and Fe in the leaves and rhizomes of the aquatic plants under consideration.

Keywords: Heavy metals; Leaves; Rhizomes; *Glyceria maxima; Phragmites australis; Typha latifolia; Phalaris arundinacea*

1. Introduction

Due to the environment pollution, in the bottom sediments, plants and municipal ecosystems, one can observe increased concentrations of different substances of an anthropogenic origin, including heavy metals [1,2]. For evaluation of the quality of reservoirs and water courses, beside bottom sediments, the littoral zone plants are used (macrophytes), which constitute one of the basic elements of evaluating the

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ecological status of the rivers [3–5]. Bioavailability and bioaccumulation of heavy metals in aquatic ecosystems are gaining tremendous significance globally [6]. Heavy metals are most harmful and currently widely examined pollutants transported in the river systems. The flowing waters most often contain some quantities of heavy metals because they are cumulated in the bottom sediments and in the sprouts of aquatic plants. The plants play a basic role in correct functioning of water ecosystems. They produce oxygen diluted in water, participate in circulation of nutritional substances, and are habitats for many water organisms. They also participate in the process of self-purification of waters and stabilize bottom sediments. Therefore, any disturbance in the aquatic plants development is hazardous for the whole ecosystem. Macrophytes reflect quite precisely the status of heavy metal pollution of water reservoirs [7–12]. The heavy metals content in aquatic plants may exceed many times their content in the surrounding water environment [8,13,14], the wide range of variability is caused by biology and ecology of particular species. Differences in accumulation of elements are observed not only among the species but also depend on the part of the plant or vegetation season. Most chemical elements are bio-accumulated in plant tissues, and the hazard of being poisoned by them within the trophic chain increases [15]. Some aquatic plants are used in remediation methods [16,17]. The plants react differently to increased concentrations of elements in the environment. Intake and bioaccumulation of necessary constituents are an element of the natural cycle [18]. Controlling the chemical composition of the littoral plants as well as bottom sediments at the municipal areas is necessary, since it allows for specification of the existing and potential hazards resulting from a toxic impact of heavy metals on water environment and human health.

The aim of the research was to evaluate the content of Zn, Fe, Mn, Ni, and Cu in leaves and rhizomes *Glyceria maxima* (Hartm.) Holmb., *Phragmites australis* (Cav.) Trin. ex Steud., *Typha latifolia* L., and *Phalaris arundinacea* L. and to compare their cumulative properties in the context of selected heavy metals in the littoral zone of the Słupia River within the limits of the city of Słupsk.

2. Material and methods

2.1. Research site

The research was carried out in summer 2013 within the area of 10 stations situated within the boundaries of the city of Słupsk (54°28´N, 17°02´E) along the Słupia River. The Słupia River is situated in the central part of Pomerania (Northern Poland), (Fig. 1). From the North, the Słupia River catchment borders the Baltic Sea catchment, from the West—the Wieprza River catchment and from the South—the Brda River catchment, and from the East—Łeba and

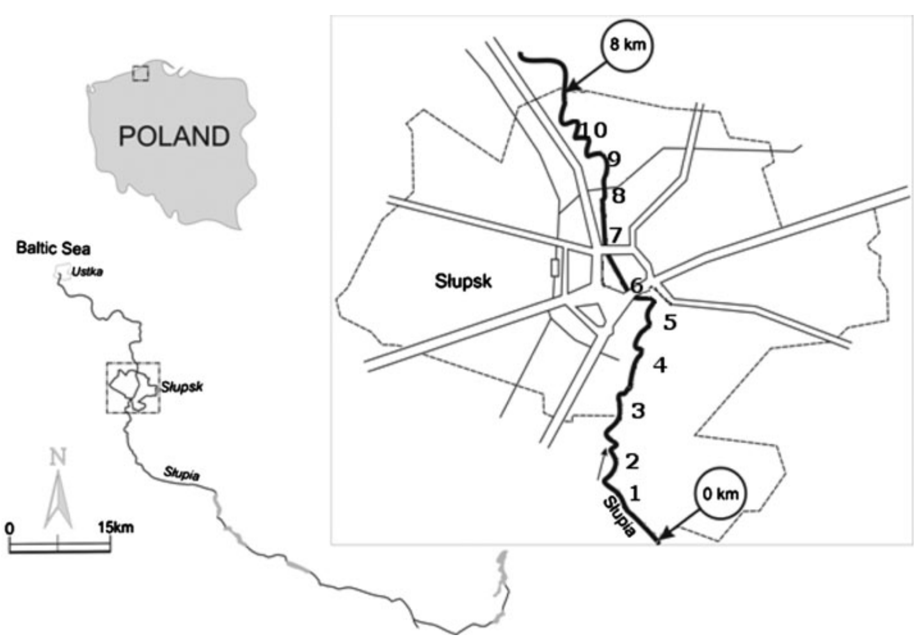

Fig. 1. Sediment and macrophytes sampling points.

Łupawa. It is a lowland watercourse of the length of 138.6 km and of the area of the catchment of 1,620 km^2. The Słupia River headwater is at the Kashubian Lake District close to Sierakowska Huta at the height of 178 m a.s.l. The width of the water bed varies from 7 m in the upper part of the river to 40 m at its mouth, where the average flow is 15.5 m/s.

The river stream is strongly meandered. The area of the city of Słupsk covers a 8 km stretch of the Słupia River, whose shores are covered with numerous macrophytes, (Table 1).

2.2. Plant sampling and methods of chemical analysis

The samples of bottom sediments and of leaves and rhizomes, *Glyceria maxima*, *Phragmites australis*, *Typha latifolia*, and *Phalaris arundinacea* (Fig. 1), originated from the littoral zone of the Słupia River. The bottom sediments were collected with the use of the *Eckman* sampler from the depth of 0–15 cm. After their transport to laboratory, the samples were dried at the temperature of 65˚C, they were sieved through the sieve of 1 mm and grinded in a mortar. In bottom sediments indicate active acidity (pH, H_2O), exchange acidity (pH, KCl), and the organic matter content—by the method of heat loss in a muffle furnace at the temperature 550˚C. The samples of macrophytes within the area of each station were taken for the tests from several plants by preparing mixed samples separately made of leaves and separately of rhizomes. After the transport to the laboratory, the plant material was cleaned of mineral parts of the soil, flushed in the distilled water, and dried to constant mass at the temperature of 65˚C. Then, it was homogenized in a laboratory grinder. The plant and bottom sediments samples were mineralized wet with concentrated nitric acid (65%) and hydrogen peroxide (30%). The concentration of Zn, Fe, Mn, Ni, and Cu in plants determined by atomic absorption spectrometry, (Aanalyst 300, Perkin Elmer). The analyses were performed in the oxy-acetylene flame. The tests were carried out following the original standards (Merck KGaA,1 g/1,000 mL). The heavy metals content in the tested macrophytes was related to physical and chemical properties of the bottom sediments (Table 2).

2.3. Statistical analysis

In order to characterize and compare concentrations of particular heavy metals in the sprouts of macrophytes, average, maximum, and minimum values were calculated with standard deviations. The relation rhizomes/leaves as to the content of Zn, Fe, Mn, Ni, and Cu in the sprouts of aquatic plants were established. The distribution of the content of the examined metals in aquatic plants was tested by means of the Shapiro–Wilk test. The saliency of the diversity of the heavy metals content in leaves and rhizomes of macrophytes was evaluated by the non-parametric Mann–Whitney U-test. For calculations, *Statistica* software was used (7.1).

3. Results and discussion

Numerous studies in Poland and abroad confirm specific cumulative properties of macrophytes in reference to many heavy metals [12,20]. The role of bioindicators of pollution of water within the municipal areas is often played by such species as *T. latifolia*, *P. australis*, as well as *G. maxima* and *P. arundinacea* [8,21–25]. The level of the heavy metals content in the sprouts of macrophytes reflects the ecological status of water ecosystems, including the bottom sediments.

Table 1
Distribution of macrophytes for researched positions

Research position	Predominant macrophytes			
	Glyceria maxima	*Phragmites australis*	*Typha latifolia*	*Phalaris arundinacea*
1	+	+	+	−
2	+	+	−	+
3	+	+	−	+
4	+	+	+	+
5	+	−	+	+
6	+	+	+	+
7	+	+	+	+
8	+	−	−	+
9	+	+	−	−
10	+	+	−	−

Table 2
Physico-chemical properties of bottom sediments of Słupia River [19]

Location	pH	Organic matter (%)	Zn (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	Cu (mg/kg)
1	8.0	1.8	23.0	8,728.0	142.7	12.7	2.6
2	8.1	0.6	17.3	4,008.0	95.3	8.7	3.8
3	7.5	0.7	26.9	11,283.3	143.5	11.7	4.9
4	7.0	7.9	50.3	14,186.7	320.1	16.4	12.7
5	7.9	0.8	22.5	6,877.7	58.1	11.0	15.1
6	8.2	0.7	12.4	6,041.3	71.3	11.0	7.4
7	8.1	2.0	22.2	7,142.0	175.1	11.6	7.5
8	7.9	0.6	13.5	4,948.0	64.0	10.7	5.4
9	8.0	1.1	104.7	14,216.7	73.9	9.5	10.1
10	7.7	5.4	47.7	15,503.3	376.7	15.7	14.0
Min	7.0	0.6	13.5	4,008.0	58.1	8.7	2.6
Max	8.2	7.9	104.7	15,503.3	376.7	16.4	15.1
Mean ± SD	7.8 ± 0.4	2.1 ± 2.5	34.1 ± 28.0	9,293.5 ± 4203.6	152.1 ± 111.5	11.9 ± 2.5	8.4 ± 4.4
CV (%)	4.6	117.0	82.3	45.2	73.3	20.8	52.8

Note: SD—standard deviation, CV—coefficient of variation.

The bottom sediments in the Słupia River within the municipal areas of the city of Słupsk were characterized by a slightly alkaline reaction with some content of organic matter (Table 2). The concentration of heavy metals in the examined bottom sediments was low and remained within the limits of the geochemical background for the majority of determined elements [26]. Only in the case of Zn, Cu, and Ni, it sporadically exceeded the level of the geochemical background at the stations in the central part of the city. According to Lawa's classification [27], the deposits of the Słupia River, due to the content of the determined heavy metals, were classified in the 1st quality class as the uncontaminated deposits.

3.1. Metals content in aquatic plants

The heavy metals' content in the bottom sediments of the rivers and the sprouts of aquatic plants reflects the impact of anthropopressure on the natural environment. The examined plant species represented diversity in accumulation of heavy metals. The highest average content of zinc was found in the leaves of *P. australis* (50.1 mg/kg) and the lowest in *T. latifolia* (21.4 mg/kg), Fig. 2. Zinc is an indispensable metal for all plants [20]. Zn content in the leaves of aquatic plants of the Słupia River was within the limits of the levels permissible for plants (10–70 mg/kg), [26] except for the stations in the central part of the city, where the leaves of *P. australis* contained slightly over 70 mg/kg Zn. Much higher zinc quantities were found in the rhizomes than in the leaves of the tested plants (Table 3). The highest concentration was reflected in the case of rhizomes of *P. australis* (68.2 mg/kg) and the lowest in *T. latifolia* (54.9 mg/kg), (Fig. 2). A similar zinc content in the sprouts of *P. australis* was indicated in the research work of Skorbiłowicz and Wiater [28]. Similar relations in zinc distribution in the aboveground sprouts and underground sprouts of various macrophytes were described in the works of Skorbiłowicz and Wiater [28], Aksoy et al. [8], Vardanyan and Ingole [6], as well as Vymazal et al. [23] and Klink et al. [12]. Root and rhizomes of *P. australis* can accumulate great amount of heavy metals because it has the cortex parenchyma with large intercellular air spaces [29]. Strong accumulative properties of *P. australis* in the relation to zinc were also confirmed by the research work of Salt and Kramer [30]. The other species, *G. maxima* and *P. arundinacea,* accumulated zinc incomparable quantities (29.1 and 29.3 mg/kg respectively). However, the rhizomes of *P. arundinacea* accumulated much more of that element (92.2 mg/kg) than in the case of *G. maxima* (59.3 mg/kg), (Fig. 2).

The surplus of zinc in the environment originates mostly from industrial emission as dust fall and by pollution of soil, waste, and municipal sewage. The zinc content in the plants of polluted habitats can be very high, especially in the leaves, rhizomes, and roots.

Among the macrophytes of the Słupia River, the largest quantities of iron were accumulated by the leaves of *P. arundinacea* (261.3 mg/kg), and the lowest quantities of that element were found in the leaves of *T. latifolia* (116.1 mg/kg). The average content of Fe in the leaves of the examined macrophytes was within the limits typical for many plants (50–250 mg/kg [26]), except for the leaves of *P. arundinacea,* (Fig. 2). At the stations 2, 3, 7, and 8 slightly over the content of Fe were

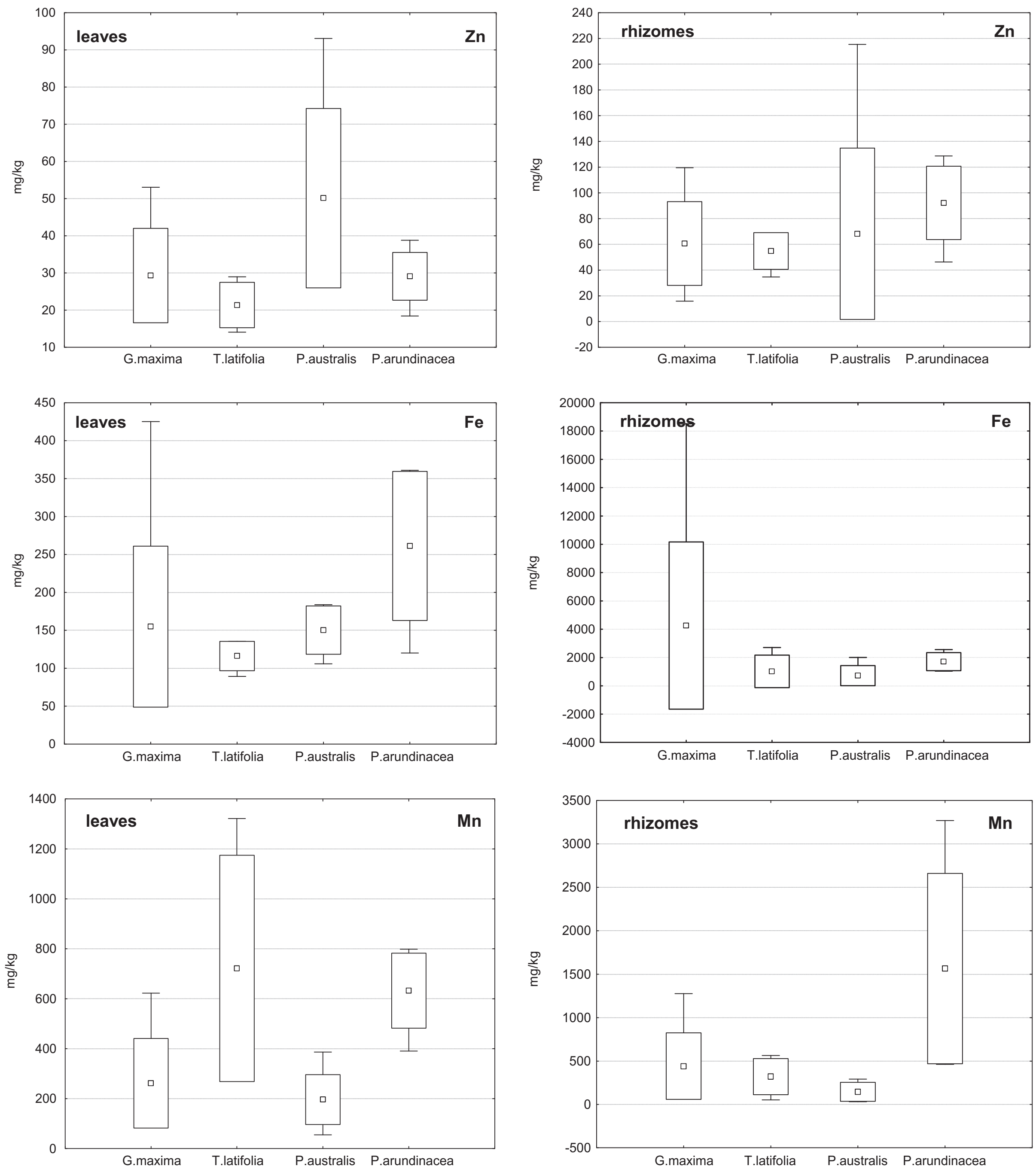

Fig. 2. Zn, Fe, and Mn concentration in leaves and rhizomes in predominant macrophytes of Słupia River. Point (mean), rectangle (standard deviation), and whiskers (minimum–maximum).

found in the leaves of that macrophyte than the value above, but lower than 360.1 mg/kg. The level of toxicity of Fe in the sprouts of plants has not been specified so far. It depends, above all, on the species. The research performed by Teuchies et al. [31] indicated that macrophytes accumulated Fe in the leaves in the following quantities: *P. australis* (194 mg/kg), *T. latifolia* (212 mg/kg), *G. maxima* (378 mg/kg), and *P. arundinacea* (499 mg/kg), which indicates strong accumulative properties in reference to iron. Under conditions of substantial environmental pollution, the leaves of macrophytes accumulate more iron, *P. australis* 420 mg/kg

Table 3
Rhizomes/leaves concentration (mean) ratios of research elements in *G. maxima*, *P. australis*, *T. latifolia* and *P. arundinacea* from Słupia River

Species	Rhizomes/leaves				
	Zn	Cu	Ni	Mn	Fe
Glyceria maxima ($n = 30$)	2.02	2.06	1.43	1.68	21.50
Phragmites australis ($n = 24$)	1.36	1.68	1.04	0.74	4.79
Typha latifolia ($n = 15$)	2.45	1.01	1.96	0.44	8.77
Phalaris arundinacea ($n = 21$)	3.17	1.68	2.16	2.47	6.53

[32] or 508 mg/kg [29]. Much higher Fe content was found in the rhizomes of aquatic plants than in the leaves of (Table 3).

The results are confirmed in the work of Demerizen and Aksoy [32]. The highest quantities of iron were found in the rhizomes of *G. maxima* (4,259.9 mg/kg) and the lowest in the case of *P. australis* (719.8 mg/kg). The high content of iron in the rhizomes of *G. maxima* can indicate accumulative properties of that species in reference to Fe. At the same time, minor concentrations in the leaves indicate existence of a protective barrier, lifting the transfer of the iron compounds from the underground to aboveground sprouts [33]. According to Kabata-Pendias and Pendias [26], Fe belongs to the low-mobility elements in a plant and is mostly gathered in a underground parts.

The highest content of manganese was found in the leaves of *T. latifolia* (721.4 mg/kg) and the lowest in *P. australis* (196.4 mg/kg), Fig. 2. According to Kabata-Pendias and Pendias [26], the plants demand for manganese is diverse, and in most cases, the sufficient level is 10–25 mg/kg. The concentration about 500 mg/kg can be toxic for most plants. The increased Mn content in the sprouts of *T. latifolia* and *P. arundinacea* indicates a positive influence of these macrophytes on purification of waters and bottom deposits of manganese compounds in relation to the physiological demand and can be a genetic feature. The average concentration of manganese in the waters of the Słupia River varied within the limits of 49.2–50.1 μg/L [34]. The experiments of Teuchies et al. [31] confirm strong accumulative properties of the leaves of *T. latifolia* in relation to manganese in comparison with other examined aquatic plants. Similar dependency in accumulation of manganese in the sprouts of *T. latifolia* was described in the study of Klink et al. [12] and Demerizen and Aksoy [32]. The highest content of manganese was found in the rhizomes of *P. arundinacea* (1,564.5 mg/kg) and the lowest in the rhizomes of *P. australis* (145.7 mg/kg), Fig. 2. Among the tested macrophytes, only *T. latifolia* and *P. australis* represented higher content of manganese in the leaves than in the rhizomes, Table 3. The remaining species accumulated larger quantities of Mn in underground sprouts.

The average content of nickel in aquatic plants of the Słupia River varied from 13.8 mg/kg in the leaves of *T. latifolia* to 22.9 mg/kg in the leaves of *P. australis* and in the rhizomes from 23.8 (*P. australis*) to 36.9 mg/kg in *P. arundinacea* Fig. 3. The strong accumulative property of those macrophytes in relation to nickel was confirmed by the research studies of Salt and Kramer [30] and Mays and Edwards [35]. The physiological content of nickel in the plants is most often 0.1–5.0 mg/kg [26], while at the areas of city agglomerations such levels are usually much higher since nickel is easily bioaccumulated, especially in aquatic plants which are sensitive bioindicators of waters. The content of Ni both in the leaves and rhizomes of the tested macrophytes exceeded the physiological demand of most of the plants, which shows little contamination of the water environment with that element. Average nickel concentration in the waters of the Słupia River varied from 2.16 to 2.38 μg/L, [34]. In all tested species of aquatic plants, Ni was accumulated in larger quantities in underground sprouts than in the aboveground ones (Table 3). The results were confirmed in the studies of Mikryakova [36], as well as Vardanyan and Ingole [6]. Nickel is easily accumulated by the plants and transported to their aboveground parts, and when in excess, it is accumulated in the roots [26]. According to Sawids et al. [29] within the area of one of the lakes in Greece, leaves of *P. australis* accumulated 20.8 mg/kg Ni and the roots 18.7 mg/kg.

The highest average copper content in the leaves of the examined plants was found in the case of *G. maxima* (10.2 mg/kg) and the lowest in *P. arundinacea* (6.6 mg/kg), Fig. 3. Much higher quantities of that element were found in the rhizomes of the macrophytes from the Słupia River, Table 3. The largest quantities of Cu were accumulated in the rhizomes of *G. maxima* (21.1 mg/kg) and the lowest in *P. arundinacea* (11.1 mg/kg). The average concentration of copper in the waters of the Słupia River varied from 2.2 to 3.5 μg/L [34]. The examined macrophytes accumulated slightly larger quantities of Cu than their physiological demand, not exceeding, however, the toxic value (>30 mg/kg), [26]. Copper in the plants is an element of little mobility; to cover physiological demand, its sufficient quantity for most plants is below 4–5 mg/kg and is substantially diversified depending on the part of the plant, its developmental stage, species, and variety. Its average content in the aboveground parts of the plants is most often from 5 to 20 mg/kg [26]. The similar copper content in the sprouts of *P. australis* was described in the studies of

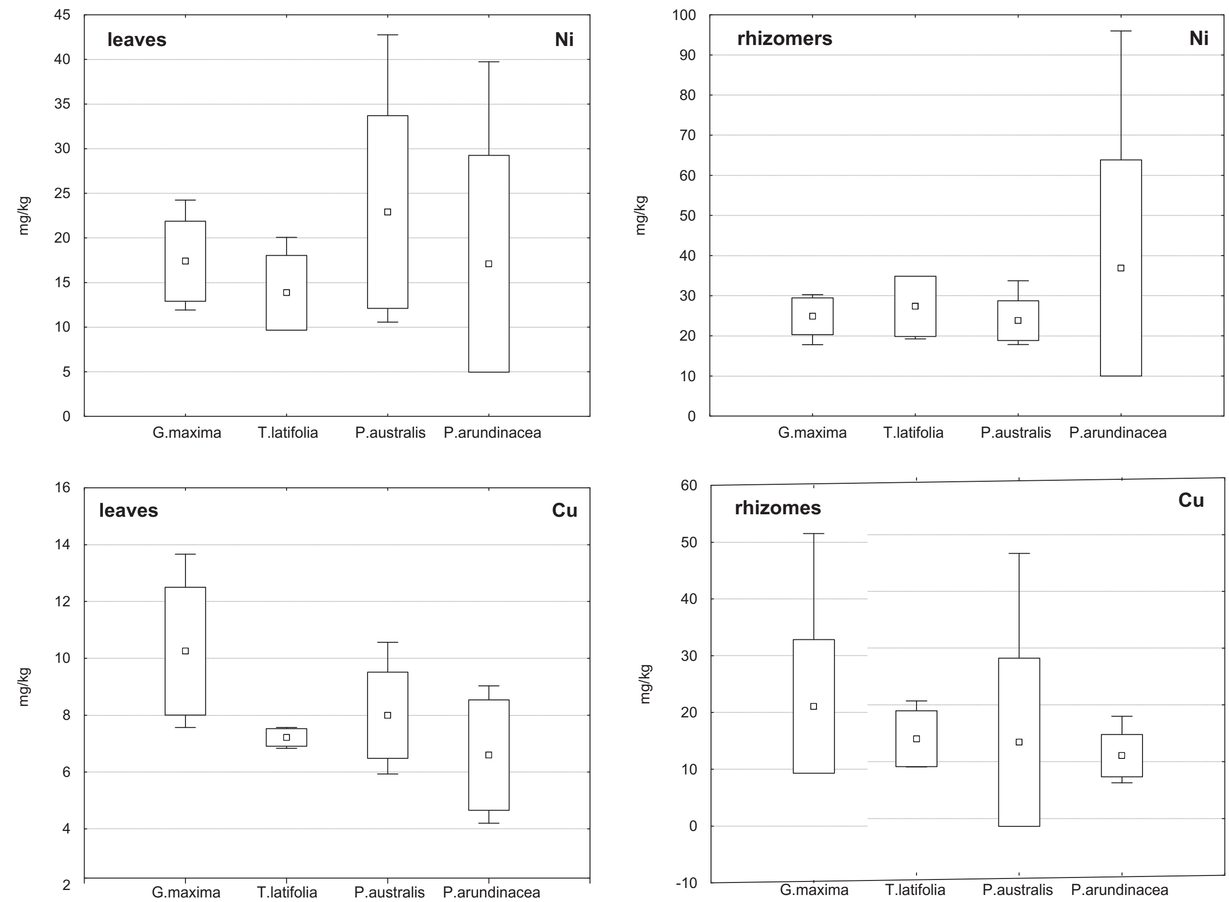

Fig. 3. Ni and Cu concentration in leaves and rhizomes in predominant macrophytes of Słupia River. Point (mean), rectangle (standard deviation), and whiskers (minimum–maximum).

Skorbiłowicz and Wiater [28]—(7.4–10.5 mg/kg), Teuchies et al. [31] from 4.2 to 6.2 mg/kg the sprouts of various macrophytes, and Klink et al. [12] from 3.7 to 4.2 mg/kg in the sprouts of *T. latifolia*.

The relationship among the contents of the determined heavy metals in the sprouts of macrophytes was identical for all examined species and could be arranged into the following successions: Mn > Fe > Zn > Ni > Cu in leaves and Fe > Mn > Zn > Ni > Cu in rhizomes. The examined plants accumulated heavy metals mainly in rhizomes, except for manganese whose highest quantities in the case of *P. australis* and *T. latifolia* were found in the leaves (Table 3).

3.2. Relationship between concentration of heavy metals in plants and in bottom sediments

Reactions of plants to the content of heavy metals in water environment as well as the stress connected with the presence of heavy metals in atmospheric dust vary. Plant dependent factors, such as the species, age, the developmental stage, ion reactions of synergic and antagonistic character as well as the impact of physiologically conditioned defense mechanisms, decide about intake of heavy metals from bottom sediments by plants [26]. The main factor deciding about the availability of heavy metals for the examined plants is the reaction of bottom sediments. Solubility of metals is low as to neutral and alkaline reactions (Table 2) and increases along with lowering of the value of pH [37]. An increase in the mobility of Zn and Mn is most effective with pH 6, Cu and Ni at pH 5.5, while Fe at pH 4. Manganese, however, is characterized by increased solubility also in alkaline environment [38].

The concentration of heavy metals in the rhizomes of the examined aquatic plants represented a series of statistically salient correlations with the content of Zn, Cu, Ni, Mn, and Fe in the bottom sediments. Along with an increase in concentration of most heavy metals in the bottom sediments of the Słupia River, an increase in the concentration of Zn and Ni in the leaves was observed and Mn and Fe in leaves and rhizomes *G. maxima* (Table 4).

The copper content in the sprouts of *G. maxima* did not represent any salient connection with the concentration of the tested metals in the bottom sediments of the Słupia River. It may be the effect of a low mobility of that element [26] and indicate some copper intake by that species mainly from the water and air along with the dust fall. The scope of concentration of Cu in the water of the Słupia River was 2.2–3.5 μg/L within the city limits [34], which slightly exceeded the natural content of Cu (1–2 μg/L) for river waters [26].

The zinc content in the rhizomes of *P. australis* was substantially connected with the concentration of Ni, Mn, and Cu in the bottom sediments of the examined river (Table 4). This is probably the result of the interaction between these elements [26]. A positive correlation between the concentration of Cu in sediments and the copper content in the rhizomes *P. australis* and the lack of a statistically significant correlation between the content of Cu in bottom sediments and leaves may indicate deposition from the atmosphere with dust and confirm a small mobility of copper in plants [34]. These relationships are consistent with the results obtained by Aksoy et al. [8,39], which indicates a relatively low mobility of Cu in aquatic plants and accumulation it in large quantities in the rhizomes and roots. The content of all heavy metals in the bottom sediments had substantial impact on the concentration of nickel in the leaves, and zinc and iron on the content of Ni in the rhizomes of *P. australis*. The most serious sources of pollution of the municipal environment of Słupsk is nickel emission in the process of combustion of liquid fuels, mostly diesel, combustion of coal and some sewage discharge [26]. Concentration of manganese in the leaves and rhizomes of that macrophyte indicated negative correlation with Mn included in the bottom sediments. Such a status indicates the intake of manganese by aquatic plants mostly from the river deposits of the Słupia River, with pH > 7 (Table 4). The lack of vital correlation between Fe content in bottom deposits, leaves, and rhizomes *P. australis* indicates low availability of iron which in alkaline environment appears usually in a form of sparingly soluble compounds [26].

A slightly different relationship among examined heavy metals was discovered in the case of *T. latifolia.* The zinc and copper content in the bottom sediments

Table 4
Results of correlation analyses for interelemental relationships in bottom sediments and aquatic plants

		Zn	Cu	Ni	Mn	Fe
		Glyceria maxima, leaves (rhizomes), $n = 30$, $p < 0.05$, $r_{crit.} = 0.31$				
Bottom sediment	Zn	−0.02 (0.19)	−0.25 (−0.12)	**0.49** (0.29)	0.27 (0.09)	0.24 (0.25)
	Cu	−0.12 (0.15)	−0.20 (−0.06)	**0.77** (−0.13)	**0.45** (**0.51**)	**0.45** (**0.55**)
	Ni	**0.43** (0.06)	0.25 (−0.15)	**0.58** (−0.04)	**0.76** (**0.77**)	**0.63** (**0.85**)
	Mn	**0.46** (−0.17)	0.18 (−0.29)	**0.59** (−0.05)	**0.87** (**0.75**)	**0.76** (**0.85**)
	Fe	**0.35** (0.06)	0.05 (−0.18)	**0.59** (−0.09)	**0.62** (**0.43**)	**0.68** (**0.58**)
		Phragmites australis, leaves (rhizomes), $n = 24$, $p < 0.05$, $r_{crit.} = 0.34$				
Bottom sediment	Zn	0.29 (0.08)	0.29 (0.08)	**−0.36** (**0.84**)	−0.18 (0.29)	**−0.57** (**0.59**)
	Cu	−0.08 (**0.36**)	0.21 (**0.49**)	**−0.46** (0.26)	−0.19 (−0.18)	**−0.35** (0.07)
	Ni	0.31 (**0.46**)	0.25 (**0.64**)	**−0.34** (−0.23)	**−0.40** (**−0.80**)	0.13 (**−0.62**)
	Mn	0.03 (**0.35**)	**0.42** (**0.52**)	**−0.55** (−0.32)	**−0.51** (**−0.65**)	**−0.35** (**−0.56**)
	Fe	0.32 (0.18)	**0.42** (0.32)	**−0.50** (**0.54**)	−0.24 (**−0.42**)	−0.23 (−0.08)
		Typha latifolia, leaves (rhizomes), $n = 15$, $p < 0.05$, $r_{crit.} = 0.44$				
Bottom sediment	Zn	**0.97** (**−0.79**)	0.28 (**−0.57**)	−0.22 (0.37)	**0.94** (0.03)	**0.44** (**−0.46**)
	Cu	**0.88** (−0.41)	0.02 (**−0.88**)	0.42 (−0.00)	**0.54** (**−0.75**)	**0.51** (−0.12)
	Ni	−0.34 (**0.58**)	**−0.79** (−0.42)	**0.91** (**0.52**)	**−0.75** (−0.22)	0.22 (−0.33)
	Mn	−0.36 (**0.62**)	**−0.81** (−0.42)	0.91 (**0.56**)	**−0.77** (−0.23)	0.17 (−0.29)
	Fe	−0.28 (**0.50**)	**−0.74** (**−0.45**)	**0.90** (**0.46**)	**−0.70** (−0.16)	0.30 (−0.39)
		Phalaris arundinacea, leaves (rhizomes), $n = 21$, $p < 0.05$, $r_{crit.} = 0.37$				
Bottom sediment	Zn	**−0.52** (**−0.74**)	**−0.44** (**−0.40**)	−0.27 (**0.50**)	**−0.53** (0.21)	**−0.52** (**−0.43**)
	Cu	0.04 (−0.07)	0.27 (−0.01)	**−0.39** (−0.34)	**−0.42** (**0.75**)	**−0.82** (**0.37**)
	Ni	**−0.72** (**−0.50**)	−0.26 (−0.13)	−0.29 (−0.17)	**−0.64** (0.15)	**−0.58** (−0.36)
	Mn	**−0.67** (**−0.74**)	**−0.52** (**−0.41**)	−0.24 (−0.35)	**−0.61** (−0.03)	**−0.37** (**−0.60**)
	Fe	**−0.56** (**−0.61**)	−0.36 (−0.28)	**−0.45** (−0.26)	**−0.46** (0.05)	**−0.40** (**−0.48**)

Note: Significant correlation are in bold.

showed strong, positive correlations with concentration of Zn in the leaves and Zn, Mn, Ni, and Fe with Zn content in the rhizomes of that macrophyte (Table 4). According to De Souza et al. [40], soluble forms Mn, Ni, and Zn in the root zone of *T. latifolia* become immobilized, which limits their availability for plants. Along with an increase in the content of iron in the bottom sediments, a decrease in the concentration of copper in the rhizomes of *T. latifolia* was discovered ($r = -0.45$). An increased Fe content in bottom sediments can have impact on lowering of assimilability of Cu by plants due to antagonism Cu–Fe [26]. The higher cooper content in the rhizomes of that macrophyte was substantially connected with the concentration of zinc and copper in the bottom sediments of the Słupia River. The nickel and iron content in the river deposits showed strong correlation coefficients with the concentration of Ni in leaves and Ni, Mn, and Fe with the content of Ni in rhizomes of *T. latifolia*. The concentration of manganese in the leaves was substantially connected with the content of all examined heavy metals in the bottom sediments of the Słupia River and the content of Mn in the rhizomes only with the concentration of Cu ($r = -0.75$), Table 4. Important statistic relationships between the concentration of manganese in the leaves of that macrophyte and its concentration in the bottom sediments were also presented in the study of Klink et al. [12]. In the case of the content of Fe in the leaves of *T. latifolia*, an important relationship was discovered with the concentration of Zn and Cu in the bottom sediments ($r = 0.44$ and 0.51). A series of statistically valid correlations between heavy metals content in bottom sediments and sprouts of *T. latifolia* were indicated by Greger [41], as well as Demirezen and Aksoy [32] in other aquatic plants.

From among tested heavy metals, only the content of Zn and Fe in leaves and rhizomes indicated statistically vital correlation coefficients with the content of these elements in bottom sediments of the Słupia River (Table 4). Zinc and iron are the elements which are characterized by high mobility and are easily accumulated in plants. [26]. Along with an increase in the concentration of Ni in bottom deposits, lowering of the content of Zn was observed in leaves and rhizomes of *P. arundinacea*, which is confirmed by negative values of correlation coefficients ($r = -0.72$ and -0.50). The excess of nickel can have a limiting impact on intake of Zn by the plants [26]. Correlation coefficients (Table 4) also indicate that the Cu and Ni content in leaves and rhizomes of *P. arundinacea* does not show any vital relation to their content in bottom sediments. The origination of these elements in sprouts of the examined species will be rather connected with atmospheric deposition. Dust fall within the area of Słupsk remained at the level from 6.8 to 11.5 $\mu g/m^3$ [42]. A series of statistically vital correlations between the heavy metals content in bottom sediments and leaves and rhizomes confirm that the species can be used in biomonitoring of environment pollution [43].

Table 5
Statistical significance of differences (U Mann–Whitney U-test)

In relation:		Zn	Cu	Ni	Mn	Fe
G. maxima–P. australis	leaves	*	*	*ns*	*ns*	*ns*
	rhizomes	*ns*	**	*ns*	*ns*	*ns*
G. maxima–T. latifolia	leaves	*ns*	**	*ns*	*	*ns*
	rhizomes	*ns*	*ns*	*ns*	*ns*	*ns*
G. maxima–P. arundinacea	leaves	*ns*	**	*ns*	**	*
	rhizomes	*ns*	*	*ns*	*	*ns*
P. australis–T. latifolia	leaves	**	*ns*	*ns*	**	*ns*
	rhizomes	*ns*	*ns*	*ns*	*ns*	*ns*
P. australis–P. arundinacea	leaves	*	*ns*	*ns*	***	*
	rhizomes	*ns*	*ns*	*ns*	**	*ns*
T. latifolia–P. arundinacea	leaves	**	*ns*	*ns*	**	*ns*
	rhizomes	*ns*	*ns*	*ns*	*ns*	*ns*

Notes: ns—no significance.
*Significance level of $p < 0.05$.
**Significance level of $p < 0.01$.
***Significance level of $p < 0.001$.

According to Greger [41], so far, many research studies have shown some vital correlations between the content of heavy metals in the sprouts of aquatic plants and the content in the bottom sediments. The correlation coefficients presented in Table 4 show that the leaves and rhizomes of the examined species of aquatic plants accumulate substantial volume of heavy metals from bottom sediments which contributes to their purification [12]. Diversification of correlation coefficients in the case of *G. maxima*, *P. australis*, *T. latifolia*, and *P. arundinacea* results, especially from differences among species and ion interactions.

Following the non-parametric Mann–Whitney U-test, the statistical saliency between the content of heavy metals in the leaves and rhizomes of the tested macrophytes was verified, Table 5. A series of statistically salient differences were shown in the content of Zn, Cu, Mn, and Fe in the leaves and rhizomes of the aquatic plant species under consideration.

4. Conclusion

The content of Zn, Cu, Ni, Mn, and Fe in the sprouts of the aquatic plants showed substantial diversity depending on the species and the type of sprout. The tested plants accumulated heavy metals mainly in rhizomes, except for manganese, which, in the case *P. australis* and *T. latifolia* appeared in larger quantities in the leaves. From among the tested species of macrophytes, *T. latifolia* accumulated the largest quantities of Zn and Ni, and *G. maxima* the largest quantities of Mn and Fe. A high content of iron in the rhizomes of *G. maxima* can indicate accumulative properties of that species in relation to Fe. At the same time, the low concentration in the leaves shows existence of a protective barrier limiting the transfer of the iron compounds from underground to aboveground sprouts. An increased content of Mn in the sprouts of *T. latifolia* and *P. arundinacea* in relation to the physiological demand can be a genetic feature and can indicate a positive impact of these macrophytes in purification of waters and bottom sediments from manganese compounds. The relationships among the content of the determined heavy metals in the spouts of macrophytes were identical for all tested species and could be arranged into the following sequences: Mn > Fe > Zn > Ni > Cu in leaves and Fe > Mn > Zn > Ni > Cu in rhizomes. The concentration of heavy metals in the examined bottom sediments was slow and remained within the limits of the geochemical background for majority of determined elements. In the case of Zn, Cu, and Ni, they sporadically exceeded the level of the geochemical background at the stations in the central part of the city. The content of examined heavy metals in the bottom sediments of the Słupia River was saliently correlated with the content of many metals both in the leaves and rhizomes of the macrophytes. The above mentioned relationships indicate many differences between the examined aquatic plants as to accumulation of metal elements in leaves and rhizomes. The differences in the relationship of the sprout of a macrophyte and the bottom sediments are due to chemical features of Zn, Cu, Ni, Fe, and Mn, as well as their bioavailability. The non-parametrical Mann–Whitney U-test showed a series of statistically salient differences in the content of Zn, Cu, Mn, and Fe in the leaves and rhizomes of *G. maxima, P. australis, T. latifolia*, and *P. arundinacea*. The macrophytes, accumulating in their sprouts substantial quantities of heavy metals, constituted an effective protective barrier for the waters and bottom sediments.

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