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BIOACCUMULATION OF HEAVY METALS IN HYDROMACROPHYTES FROM FIVE COASTAL LAKES (NORTH-WESTERN POLAND, BALTIC SEA)

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Abstract

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The study concerned Polish coastal lakes separated from the Baltic Sea by a sandbar. The study was designed to determine whether the aquatic plants in the coastal lakes in Poland accumulate Cu, Ni, Cd. The material consisted of water and aquatic plant samples collected in the years 2012 and 2013 in lakes Resko Przymorskie, Jamno, Bukowo, Kopań and Wicko.
The metal with the lowest content ($mg.kg^{-1}$) in the plants was Cd, and the concentrations can be arranged as follows: Cd < Ni < Cu (mean 0.46 < 1.91 < 5.56) in 2012 and (mean 1.04 < 1.86 < 4.68) in 2013. For water, the order of concentrations ($mg.l^{-1}$) of metals was follows: Cd < Ni < Cu (mean 0.0010 < 0.0033 < 0.0035) in 2012 and Cd < Cu < Ni (mean 0.0036 < 0.0107 < 0.0115) in 2013. The metal bioaccumulation in hydro-macrophytes expressed by means of a bioaccumulation factor (BCF) was as follows: Cd < Ni < Cu (mean 474 < 1447 < 1519) in 2012 and Ni < Cd < Cu (mean 201 < 369 < 542) in 2013.
The metal concentrations in samples were found comparable with those in moderately polluted surface waters. Statistically significant regression was only found between Cd concentration in water and in plants ($R = 0.3484$). Conductivity does not affect metals content in samples. Statistically significant differences were noted between water reaction and the content of all metals in water, and Cd content in case of the plants.

Keywords: coastal lakes, aquatic plants, water, heavy metals, bioaccumulation, hydrochemistry, hydrobiology

INTRODUCTION

Surface waters, such as lakes, tend to accumulate pollution from catchment areas. The chemical composition of the water in coastal lakes is a resultant of the inflowing river water, which collects agricultural, industrial and domestic sewage, and the Baltic Sea water that finds its way into the lakes. Coastal lakes are separated from the Baltic Sea by a sandbar. Fresh lake water and seawater mix through to canals, which are sometimes blocked (filled up with sea sand brought in by the water). For most of the year seawater has a considerably weaker impact on the quality of lake water than any pollution coming in from the land. The impact becomes more visible during periodical seawater ingression, which occurs as a result of changes in hydrological and meteorological conditions (winds during storms, etc.) (Cieśliński, 2005). The coastal lakes in Poland's Baltic belt are used for recreational purposes (cruise ships, motor boating sports, fishing). Tourist facilities in lakes catchment areas constitute an additional source of pollution, particularly noticeable in the summer.

Aquatic plants are a filter for pollutants brought into surface waters, contribute to the cleaning of aquatic environments. Thanks to metals accumulation ability, the rush vegetation growing in the shore areas of the coastal lakes help to neutralise some pollutants that reach the lakes. Thanks to its bio-accumulation capability, littoral vegetation constitutes a living barrier against the flow of pollutants from adjacent agricultural and recreational areas. The metal bioindication of aquatic plants are linked to their location in the reservoir. The way in which metals are drawn by submergent and emergent plants varies slightly. Rooted plants absorb metals from the water, bottom deposits and precipitation, while in the case of non-rooted plants the composition of the deposits has no direct bearing on the metal accumulation process (Bonanno and Giudince, 2010, Mazej and Germ, 2009, Mishra *et al.* 2008, Nguyen *et al.* 2005).

The quality of lake water depends on a number of external factors, as well as on the changes that take place in the waters themselves. Seaside lakes represent special water reservoirs. Although they are influenced by land watersheds, their content differs from that of inland lakes due to the contact with the waters of the Baltic Sea. The chemical composition of the lake water has a significant impact on plants' capability to draw metals from their natural environment. The metal drawing process is affected by the water reaction and its mineralisation. Acidic environments are conducive to the release of metals from bottom deposits and consequently boost their concentration in water. Water mineralisation, expressed as electrolytic conductivity, indicates that water carries plenty of mineral compounds. It contains calcium and magnesium carbonates, but also chlorides and sulphates (Cieśliński, 2005).

The catchment of all examined lakes is an agricultural area, and thus it may be supposed that heavy metals are present in the reservoirs, and their source are mainly plant protection products and agricultural run-offs. Additionally, some of the lakes are also affected by non-agricultural factors. Lake Jamno is situated in a close vicinity of Koszalin (110,000 citizens). Lakes Jamno and Bukowo are the receivers of sewage from the treatment plant, and Lake Wicko is localized at the direct vicinity of military airport. Because of the typically agricultural nature of the catchment areas of the coastal lakes under study, the following three metals: cadmium, copper and nickel, were chosen to characterise them. Up to that time no complete study of these lakes was conducted in the same time during two years. Only individual lakes were tested. Thanks to these studies we will see the image of lakes pollution with heavy metals in a large area of West Pomerania. Thus, the aim of the study was to determine the content of heavy metals in lake water and aquatic plants growing in the lakes depending on catchment nature and water reaction. This allowed to establish the relationship, whether water reaction and electrolytic conductivity affect heavy metals level in water and hydromacrophytes. Thus, it was possible to determine the degree of their bio-accumulation in aquatic plants. It will be possible to assess the quality of the aquatic environment of the coastal lakes in question.

MATERIALS AND METHODS

The study focused on five lakes in the Polish coastal belt of the Baltic that have agricultural catchment areas. All the lakes are separated from the Baltic by a woodland strip and have direct contact with the sea via canals. Because of the similarity of the type of catchment area (an agricultural-and-woodland catchment area), the pollutants that reach all the lakes are very similar in nature. The research was conducted in the following coastal lakes: Resko Przymorskie, Jamno, Bukowo, Kopań and Wicko (Fig. 1). The morphometric properties of the lakes are presented in Table I (Jańczak, 1997).

The study material comprised samples of water and aquatic plants taken from the littoral zone of coastal lakes in 2012 and 2013 once in each the year, in August. Water was sampled with a 3 dm^3 Ruttner water sampler (KC – Denmark A/S) into polyethylene bottles, and subsequently filtered using 0.47 glass microfiber filters Whatman. The samples (four from each site, each year) were checked for pH (PN-90/C-04540/01) and electrolytic conductivity (PN-EN 27888:1999) using Elmetron pH/conductivity meter CPC-411. The water was mineralised (acidified) with concentrated HNO_3 (Nitric acid min. 69% puriss. P. a, Reag. ACS, Reag. ISO) (Sigma-Aldrich) with proportion of acid to water (1:5). Total Cu, Ni and Cd concentrations were determined using atomic absorption spectrophotometry by means of a Varian Spectr AA-110/220 unit (Varian, Australia) (Test procedure PB-10/I). The results are given in $mg.l^{-1}$.

Whole aquatic plants (four from each site, each year) were taken randomly from each site. Collected emergent plants present on the sites. This was to show the concentration of metals in all the plants present in the lakes, not just in selected species. Collected aquatic plants (7 species: *Phragmites australis, Typha angustifolia, Glyceria maxima, Scirpus lacustris, Juncus bulbosus, Alisma plantago-aquatica, Sparganium erectum*). After being sampled, aquatic plants were thoroughly rinsed to remove dirt, first with water from the lake and then three times with re-distilled water. Afterwards they were dried at room temperature until air-dry. Whole plants were pre-ground by crushing and then being homogenised. The resultant material (0.5 g) was then placed in a Teflon HP500 vessel. After adding 5 cm^3 of HNO_3 (Nitric acid min. 69% puriss. P. a, Reag. ACS, Reag. ISO) (Sigma-Aldrich) to the sample, it was left at an ambient temperature for 24 hours, because plants were hard. Next, it was placed in Mars 5 microwave oven (CEM, USA) (Tab. II). After being cooled to an ambient temperature, the mineralysates were transferred to test tubes and diluted with re-distilled water up to 0.25 L. The concentrations of total metal (Cu, Ni, Cd) were determined using atomic absorption spectroscopy (AAS) by means of a Varian Spectr AA-110/220 unit (Varian, Australia) (Test procedure PB-10/I).

The correctness of the analytical procedures was verified using the Certified Reference Material BCR No. 60 (*Lagarosiphon major*) (The Commission of the European Communities, The Community Bureau of Reference – BCR).

LOD (limit of detection) based on the results for blank samples ($\bar{x}$ – mean of 10 blank samples, SD – standard deviation)

$$LOD = \bar{x} + 3 \cdot SD$$

The bioconcentration factor (BCF) for metals in the plants was determined as a ratio of metal contents in each plant species C_{MP} (mg.kg^{-1}) to metal concentrations in the water C_{MW} (mg.l^{-1}) (Nguyen *et al.* 2005).

$$BCF = C_{MP}/CM_{W}$$

Statistical analysis were performed using the Statistica 12, SAS 9.2 (SAS Corporation, Cary, N.C., USA) and R 2.12.1 statistical packages. Initial statistical analyses of metals content for normality using Shapiro-Wilk test revealed that data does not have normal distribution. Hence, the comparison of average metals content in analyzed groups was analyzed post hoc with the Kruskal-Wallis test. Regression analyses was used to find the importance of metals concentration in water and aquatic plants and in pH and conductivity depending on the nature of the catchment (P – nearly without pollution, A – agriculture, STP – vicinity of sewage treatment plant, MA – vicinity of military airport). PCCA diagram was prepared for the samples grouped depending on water pH: 1 – up to pH 6.49, 2 – pH 6.50–7.50, and 3 – above pH 7.50.

RESULTS AND DISCUSSION

Chemical reaction and electrolytic conductivity

Most of the studied waters have a neutral reaction, and so they have no impact on the release of any additional amounts of metals from the deposits. The chemical reaction of the water samples ranged from pH 6.32 to pH 8.55 (Tab. III). Throughout the period covered by the study, the two lowest reaction values for the two years covered by the study were determined for Lake Jamno. The highest water reactions during the two research cycles were found for Lake Bukowo, in the sample taken near the canal between the lake and the Baltic Sea. However, its significant effect on plants condition was not observed. Such an environment is also more favourable to the growth of aquatic plants. In such conditions no reduction in the number of species, no degeneration and no dying out of individual plants are observed.

Water conductivity measured in lakes, whose water mixes with seawater, indicates whether the Baltic water influences the mineralisation of the lake water and to what extent. The water's electrolytic conductivity oscillated between 456 µS·cm^{-1} and 6352 µS·cm^{-1} (Tab. III). The lowest conductivity was measured for water sampled from Lake Wicko and the highest one – from Lake Bukowo. In Lake Resko Przymorskie throughout the two year period covered by the study it exceeded 5000 µS·cm^{-1}. Seawaters inflow to the examined lakes is not systematic, the connecting channels were often filled with the sand. Thus, the values of conductivity are often mainly an effect of river waters inflow from the catchment, and do not result from Baltic seawaters inflow to the lakes.

Heavy metals in water

The heavy metal content in the surface water concerns both the water and the biotic/abiotic components. The levels of the selected heavy metals, i.e. Cu, Cd and Ni varied in the waters of the investigated lakes. In first year of the study all concentration of metals were lower than in second year. In second year (2013) a lot of rains were noted in the lake basin. So metals could be remove for example from soils. The Cu content in the coastal lake water oscillated between 0.0002 mg.l^{-1} and 0.0123 mg.l^{-1} (Tab. IV). The lowest content was observed in the second year of the study in Lake Bukowo. The highest level was found in Lake Kopań. In 2012, the Cu content was much lower than in 2013. The Cu content in the Lakes Jamno and Bukowo was higher during 2012 and 2013 than that in the remaining reservoirs under study.

Similar concentrations of copper have been found in surface water reservoirs in Poland and around the world under the influence of anthropogenic activity, as in the coastal lakes. In the years 2002–2003, a study was conducted of the water of Lake Jamno; the new study shows that Cu concentration has not changed since then (Senze and Marek, 2004). A similar type of catchment area (agricultural and woodland) and the use for, among other things, recreational, angling and pisciculture, may have a decisive impact on the similarity of concentrations. In studies covering lakes and dam reservoirs in western Poland, characterised by a comparable degree of anthropopression (Senze *et al.* 2009, Szymanowska *et al.* 1999). Furthermore, tests of water from mine reservoirs in Asia lakes in industrial, urbanised regions gave comparable ranges of values (El-Khatib and El-Sawaf, 1998, Hassan *et al.* 2010, Mishra, 2008, Yang *et al.* 2002).

Lake Gardno, also located in the west of the coastal belt, which has an agricultural-and-woodland catchment area, has water with a lower Cu content than the five lakes studied (Trojanowski and Antonowicz, 2011). Lower concentrations might be expected in areas in which anthropopression is not a risk factor and in areas subjected to – at least partial – protection. Such environments are described for European lake regions, both in mountainous and lowland areas (Mazej and Germ, 2009).

The Ni content in the water ranged from 0.0005 mg.l^{-1} to 0.0061 mg.l^{-1} (Tab. IV). The lowest value was determined for Lake Resko Przymorskie, while the highest – for Lake Bukowo. At all sampling sites in Lake Bukowo, the Ni content was higher than at the other sampling sites.

Similar values of Ni in water have been determined for water sampled from lakes in south-western Poland having greatly anthropogenically transformed (mining) catchment areas (Samecka-Cymerman and Kempers, 2001). Also, in the case of lake location in west of Poland where waters carry agricultural pollutants, the range Ni concentration in water is similar to that of the coastal reservoirs (Szymanowska *et al.* 1999). Lower contents have been discovered in samples from mountain lakes and dams reservoirs. Such catchment areas are subject to anthropogenic influences, but they are not as strong as to significantly increase the amount of nickel in water. The lake are partly subjected to protection, but also are home to tourism and recreation (Mazej and Germ, 2009).

The highest Cd concentration in water was determined for Lake Jamno (0.0256 mg.l^{-1}) and the lowest concentration was observed for Lake Bukowo – 0.0016 mg.l^{-1} (Tab. IV). The Cd content in Lakes Jamno and Lake Bukowo was higher than that in the remaining reservoirs under study.

Cadmium concentrations in water similar to those found in the lakes covered by this study were determined for water sampled from Lake Jamno in the years 2000–2003 (Senze and Marek, 2004). Lakes with typically anthropogenic catchment areas in Europe, Asia and Africa also turn out to have approximately the same range of Cd concentrations (El-Khatib and El-Sawaf, 1998, Hassan *et al.* 2010, Samecka-Cymerman and Kempers, 2001, Szymanowska *et al.* 1999). Also in reservoirs of stagnant or flowing water with an agricultural or agricultural-and-woodland catchment area, but with a relatively small load of anthropogenic pollution, located in the south or north of Poland, the concentrations found were more or less the same (Pokorny *et al.* 2015). Higher concentrations have been found in reservoirs in urbanised ones in waters of the mine reservoirs studied by Mishra *et al.* (2008) had much higher concentrations than those found in the coastal lakes. Lower concentrations have been found in piedmont and mountain waters, both flowing and stagnant, studied by Senze *et al.* (2009). Also, dam reservoirs of stagnant water various types of catchment areas, but not strongly affected by anthropopression, had a lower Cd content than the coastal lakes (Klink *et al.* 2013).

Heavy metals in aquatic plants

Heavy metal content in aquatic plants and bioconcentration factor (BCF) are presented in Table V.

In 2012, the Cu content in the macrophytes sampled ranged from 0.15 mg.kg^{-1-1} in *Phragmites australisPhragmites australis Phragmites australis* from Lake Bukowo to 19.76 mg.kg^{-1-1} in*Scirpus lacustris P.australis* from Lake Kopań, and in 2013, in *P.australis* from 1.12 mg.kg^{-1-1} Lake Wicko to 10.11 mg.kg^{-1-1} at Lake Resko. During 2012–2013, the lowest Cu levels in the lakes in question were found in Lakes Bukowo, Wicko and Resko Przymorskie, and the highest ones in Lakes Jamno and Kopań. The bioconcentration factor for Cu in aquatic plants collected in 2012 oscillated between 45 (Lake Bukowo) and 4803 (Lake Wicko). In the second year of the period, the minimum value was higher than that determined for 2012, and amounted to a BCF = 30 (Lake Kopań). The highest values were found for Lake Wicko – BCF = 1288.

The metal content in plants of coastal lakes varied significantly. Ranges of Cu values comparable to those found in the case of the coastal lakes were determined by Senze and Marek (2004) for *P. australis* from Lake Jamno, tested in the years 2002–2003. Klink *et al.* (2009) also discovered similar values in the case of *T. latifolia* – an emergent plant growing in Lake Wielkie having agricultural-and-woodland catchment areas. Also *Scirpus grossus* from a lake in Malaysia which is mainly used for recreation have a similar Cu content (Ebrahimpour and Mushrifah, 2008). Many species of emergent plants growing in lakes with urbanised catchment areas, have Cu levels similar to those found in coastal plants (Samecka-Cymerman and Kempers, 2001, Szymanowska *et al.* 1999).

Higher Cu concentrations have been found in *P.australis* and *T.latifolia* sampled from a volcanic lake in southern Italy and from reservoirs in strongly industrialised regions of Russia and Syria (Baldantoni *et al.* 2009, Hassan *et al.* 2010, Hozhina *et al.* 2001, Mishra *et al.* 2008). Lower contents, falling within the range from 0.36 mg.kg^{-1-1} to 3.60 mg.kg^{-1-1}, were found in *P.australis* in Lake Jamno in the 1990s (Modzelewski, 1996). The Cu bio-accumulation capability in Lakes Wicko, Bukowo, Jamno and Resko Przymorskie was most probably dependent on two main factors. First – water salinity, second – a more pronounced presence of anthropogenic pollutants. The fact that seawater is pushed into the lakes through canals during a backwater is a natural phenomenon and humans exert no significant influence on its intensity (the only option would be to block the canals). Water with a higher salinity is to be found in the coastal sandbar zone and this is where the copper accumulation process was the most intense. The impact of the agricultural catchment area, which is the main source of pollutants from land, was not as strong as that of seawater. Also no effect of direct vicinity of sewage treatment plant on Lakes Jamno and Bukowo was observed. Furthermore, during the summer, when the study was conducted, the coastal zone may also be affected by pollutants associated with recreational activities. A similar accumulation capability was displayed by aquatic plants (mainly *P.australis*) sampled nearly ten years earlier from Lake Jamno (Senze, Marek, 2004). This indicates a similar intensity of Cu bioaccumulation in plants of the coastal lakes. Studies carried out in the south of Poland, covering a lowland storage reservoir with a typically agricultural catchment area, just like that of the coastal lakes, have shown similar BCF values (Senze *et al.* 2009).

The Ni content in aquatic plants collected in 2012 ranged from 0.13 $mg.kg^{-1}$in *S.lacustris* from Lake Wicko to 9.12 $mg.kg^{-1-1}$, also in *S. lacustris*, from Lake Kopań. The highest values were measured for Lakes Jamno, Bukowo and Kopań, and much lower Lakes Wicko and Resko Przymorskie. The highest Ni content in plants in 2013 reached 4.44 $mg.kg^{-1-1}$ in *Typha angustifolia* from Lake Jamno. The lowest BCF for Ni for plants sampled in 2012 was 38 at the site Kopań in *S. lacustris*. The maximum BCF value, amounting to 4762 (Lake Bukowo). The highest BCF in the second year of the project was established for Lake Bukowo. It amounted to 1139 (*P.australis*). The lowest values were determined for plants from Lake Wicko (BCF = 3).

The Ni levels in macrophytes growing in water reservoirs depend on a number of factors, including water composition, precipitation and Ni content in bottom deposits. The studies did not determine the impact of Ni accumulated in bottom deposits, as these were not the subjected of the studies. Most probably, however, they had a bearing on the Ni content in plants, especially rooted ones (Mazej and Germ, 2009). Similar amounts of Ni in emergent plants (mainly common reed) have been found in Lake Jamno, which was studied in the years 2000–2003 by Senze and Marek (2004). This was also noted in the case of above discussed Cu content. Approximately the same Ni content was also found in *T.latofolia* from a lake used for recreation in the south-west of Poland, whose catchment area had a typically agricultural-and-woodland nature (Klink *et al.* 2009). The Ni content in stagnant water reservoirs, whose catchment areas have a medium degree of urbanisation and a strong degree of industrialisation, was similar to that in the coastal lakes (Samecka-Cymerman and Kempers, 2001, Senze *et al.* 2009, Szymanowska *et al.* 1999). In a lake in Syria, with an agricultural and urbanised catchment area subject to anthropogenic activities, the Ni level in emergent plants (*P.australis* and species from the genus *Typha*) was higher than that in macrophytes from Poland's coastal lake zone (Hassan *et al.* 2010). Also, studies conducted by Hozhina *et al.* (2001) in strongly industrialised regions in Russia showed a raised Ni level in *T.latifolia* in comparison to that of the coastal lakes. In Lakes Kopań, Bukowo, Jamno and Resko Przymorskie, Ni was accumulated the most intensively in plants growing in places closest to the sea belt. The seawater may have been the decisive factor behind boosting the bio-accumulation capacity of the plants. A similar bio-accumulation level was displayed by the plants from Lake Jamno in the years 2000–2003 (Senze and Marek, 2004). Consequently, it may be assumed that the load of lake waters with nickel has not changed much over the last several years. A similar BCF characterised the macrophytes from a dam reservoir in the south of Poland, whose catchment area – similarly to that of the coastal lakes – is definitely agricultural (Senze *et al.* 2009).

The highest Cd content (1.74 $mg.kg^{-1-1}$) in 2012 in macrophytes was discovered in *T.angustifolia* from Lake Kopań and in 2013–1.98 $mg.kg^{-1}$ in Lake Wicko. In the first year of the study, Cd bioaccumulation reached the highest value of 1590 (*T.angustifolia*). The lowest BCF (BCF=10) was noted for *S.lacustris*. In the second year of the study, the BCF ranged from 83 (*P. australis,* Lake Resko Przymorskie) to 1121 *(T.angustifolia,* Lake Jamno).

Like in the case of Cu and Ni, similar Cd concentrations were found in the hydromacrophytes from Lake Jamno, which was studied earlier by Modzelewski (1996) and Senze and Marek (2004). A similar Cd level was quoted *P. australis* and *T. latifolia* growing in lakes in the north and west of Poland, with a lowland-and-agricultural catchment area (Klink *et al.* 2013, Szymanowska *et al..* 1999). Approximately the same values were found for above-the-surface plants from a dam storage reservoir providing water to an urban agglomeration with an agricultural catchment area in Poland (Senze *et al.* 2009). A more or less the same Cd content was found in submergent plants from a lake in Malaysia used for recreational purposes (angling, tourism), but located in an industrialised catchment area (mines) (Ebrahimpour and Mushrifah, 2008). The situation was similar in other reservoirs (Hassan *et al.* 2010, Hoshina *et al.* 2001, Mishra *et al.* 2008, Samecka-Cymerman and Kempers, 2001).

Cadmium contents lower than those given for the plants from Poland's coastal lakes were stated by Klink, *et al.* (2009) for *T.latifolia* growing in the eutrophic Lake Wielkie in western Poland. Also *P.australis* sampled in Egypt from reservoirs with various types of management were characterised by a more or less the same range of Cd concentrations (El-Khatib and El-Sawaf, 1998). High Cd contents were also found in submergent plants from a lake in Malaysia used for recreation (angling and water tourism), but with a catchment area subject to strong anthropogenisation (mining) (Ebrahimpour and Mushrifah, 2008). In the case of Ni and Cu, the values were the highest for plants growing on the banks closest to the Baltic and to tourist towns and villages. Similar BCFs were established for Lake Jamno, studied by Senze and Marek (2004) in the years 2000–2003. Lower factor values were determined for dam reservoirs in Lower Silesia having agricultural-and-woodland catchment areas (Senze *et al.*. 2009).

Statistical Analysis

Statistically significant regression was only found between concentration of Cd in water and in plants (R = 0.3484). Electrolytic conductivity does not affect the content of metals in water and plants (Fig. 2). Water reaction affects the form of metals occurrence and its bioavailability. Thus, their content in the plants depends on water pH (Fig. 2). Statistically significant differences between water pH and examined parameters are presented in Table VI.

Statistically significant differences between the analyzed years were found in case of pH, the content of all metals in water and Cd content in the case of plants (Tab. VII).

Different relationship between water pH and conductivity was demonstrated in so called clean region, where the regression curve was presented using the equation = 6258.65–651.3·pH. This was the only case of inverse relationship of conductivity and pH (Fig. 2).

PCCA diagram (Fig. 3) points a significant role of water pH and conductivity, which was also reflected in the value of correlation coefficient (Tab. VIII).

Division of samples on 3 groups depending on pH demonstrated, that the values for multiple comparisons for conductivity, pH and Ni content in water differed statistically significantly ($P < 0.05$) (Kruskal-Wallis test) between each of the groups. In turn, in case of cadmium and copper content in the plants, the differences were found between group 2 and 3. Copper in water only differed between group 1 and other ones.

Nature of the catchment presented in PCCA diagrams allows to suppose, that this factor may be significant, and statistical significance was confirmed in case of all parameters, except Cd content in water, by an examination of p value for multiple comparisons – Kruskal-Wallis test.

With respect to the level of metals present in the examined material, statistically significant difference (R = 0.3484) was only found between the Cd content in water and plants. This can be explained, e.g. by Cd antagonism with respect to Cu. Different relationship of conductivity and pH was noted depending on the nature of catchment area (Fig. 2). In the case of the catchment not exposed to the additional pollutants (P) an inverse relationship of conductivity and pH was observed (conductivity = 6258.6531–651.3618·pH) with respect to all other catchments and in the studies concerning the samples from all areas in total.

PCCA and Kruskal-Wallis test, demonstrated statistically significant differences ($p < 0.05$) between the nature of the catchment for its various types and for particular examined parameters (Tab. IX), and interestingly, the differences between the catchments concerning e metals content in water do not coincide with metal concentration in the plant. In this case, the most likely pH and the presence of bioavailable forms is crucial in the concentration of metals in plants .

The level of Cu and Cd in the plants depends on water pH (Tab. X). Relationships observed as a result of statistical analysis concerned the values of pH and concentration of all examined metals (Cu, Ni, Cd) in water. Such relationship also included Cd level in plants.

I: *Morphometic properties of coastal lakes (Jańczak, 1997)*

Morphometric index	Jamno	Bukowo	Kopań	Wicko	Resko Przymorskie
Latitude	N54°16'24"	N54°20'35"	N54°22'04"	N54°32'22"	N54°08'32"
Longitude	E16°09'02"	E16°16'43"	E16°27'02"	E16°37'08"	E15°22'37"
Area (ha)	2239.60	1747.40	789.70	1058.90	577.10
Volume (m^3)	$3.153·10^3$	$32.071·10^3$	$14.773·10^3$	$28.495·10^3$	$7.703·10^3$
Mean depth (m)	1.40	1.80	1.90	2.70	1.30

II: *Scheme of the mineralization process*

Stage	Power		Ramp [min]	Pressure [PSI]	Temperature [^oC]	Hold [min]
	[W]	%				
1	600	50	5	60	85	5
2	300	80	15	85	115	10
3	300	70	15	170	180	15

III: *Reaction (pH) and electrolytic conductivity (μS·cm⁻¹) in the water of the coastal lakes in 2012 and 2013*

Site	Reaction		Electrolytic conductivity	
	2012	2013	2012	2013
	min–max mean±SD			
Jamno	6.37 – 6.89 6.64±0.25	6.32 – 7.09 6.64±0.28	698 – 1331 1015±262	783 – 1260 989±219
Bukowo	7.52 – 8.55 8.10±0.33	7.32 – 8.26 7.91±0.34	2854 – 6352 3716±1428	2500 – 5630 3417±1337
Kopań	6.98 – 7.61 7.20±0.28	6.63 – 7.26 7.03±0.21	1421 – 1990 1633±262	1446 – 2013 1659±266
Wicko	6.80 – 7.26 7.05±0.17	6.79 – 7.00 6.89±0.07	500 – 2055 1237±673	456 – 1974 1097±624
Resko Przymorskie	6.90 – 7.71 7.50±0.43	6.91 – 7.69 7.19±0.29	5214 – 5916 5665±336	5580 – 5814 5666±109

IV: *Copper, nickel and cadmium (mg.l⁻¹) in the water of the coastal lakes in 2012 and 2013*

Site	Cu		Ni		Cd	
	2012	2013	2012	2013	2012	2013
	min–max mean±SD					
Jamno	0.0026 – 0.0074 0.0050±0.0017	0.00130 – 0.0085 0.0118±0.0013	0.0009 – 0.0016 0.0022±0.0005	0.0013 – 0.0053 0.0234±0.0345	0.0098 – 0.0256 0.0016±0.0019	0.0097 – 0.0136 0.0020±0.0004
Bukowo	0.0026 – 0.0046 0.0035±0.0005	0.0002 – 0.0088 0.0142±0.0058	0.0009 – 0.0013 0.0058±0.0057	0.0052 – 0.0061 0.0179±0.0306	0.0016 – 0.0165 0.0012±0.0002	0.0085 – 0.0251 0.0055±0.0003
Kopań	0.0016 – 0.0063 0.0039±0.0018	0.0006 – 0.0123 0.0088±0.0014	0.0007 – 0.0013 0.0039±0.0044	0.0030 – 0.0045 0.0112±0.0019	0.0085 – 0.0138 0.0010±0.0002	0.0071 – 0.0110 0.0038±0.0004
Wicko	0.0014 – 0.0028 0.0020±0.0005	0.0006 – 0.0009 0.0072±0.0010	0.0007 – 0.0012 0.0008±0.0001	0.0015 – 0.0035 0.0088±0.0018	0.0061 – 0.0112 0.0009±0.0001	0.0056 – 0.0085 0.0026±0.0007
Resko Przymorskie	0.0014 – 0.0032 0.0024±0.0006	0.0007 – 0.0120 0.0087±0.0010	0.0005 – 0.0010 0.0048±0.0046	0.0023 – 0.0048 0.0106±0.0010	0.0091 – 0.0123 0.0014±0.0020	0.0076 – 0.0108 0.0033±0.0010

V: *Content of copper, nickel and cadmium (mg.kg⁻¹) and bioaccumulation factor (BCF) in the aquatic plants of lakes in 2012 and 2013*

Site	Cu		Ni		Cd	
	2012	2013	2012	2013	2012	2013
	min–max					
Resko Przymorskie	2.59 – 5.42 291 – 1171	3.12 – 10.11 405 – 981	0.45 – 1.16 46 – 949	0.89 – 2.11 90 – 208	0.01 – 0.05 15 – 61.7	0.37 – 1.96 83 – 760
Jamno	1.53 – 16.17 557 – 2487	2.10 – 6.03 169 – 519	1.25 – 6.49 223 – 1203	0.19 – 4.44 15 – 339	0.02 – 1.34 14 – 1203	0.40 – 1.70 188 – 1121
Bukowo	0.15 – 3.14 45 – 1185	2.89 – 5.28 183 – 596	0.98 – 2.25 251 – 4762	0.39 – 3.52 27 – 1139	0.02 – 0.36 21 – 236	0.51 – 1.12 96 – 196
Kopań	1.69–19.76 30–3025	2.12–8.41 308–1004	0.29–9.12 38–11531	0.46–3.83 37–315	0.06–1.74 86–1529	0.67–1.28 198–316
Wicko	0.52–13.74 781–4803	1.12–7.77 187–1288	0.13–3.13 180–3838	0.03–4.36 3–390	0.01–1.52 10–1590	0.57–1.98 177–932

VI: *Statistical significance of the differences between examined parameters*

Parameter		pH			Electrolytic conductivity		
		Range Amount					
		below 6.50 N=27	6.50–7.50 N=178	above 7.50 N=51	below 1000 N=68	1000–1500 N=74	above 1500 N=112
pH	water				6.79 a	6.84 b	7.40 ab
Electrolytic conductivity	water	992.15 ab	1651.53 ac	3751.92 bc			
Cu	water	0.0100 ab	0.0064 a	0.0067 b	0.0069	0.0067	0.0067
	plant	5.02	5.24 a	4.66 a	5.27	5.59	4.68
Ni	water	0.0113 ab	0.0075 ac	0.0049 bc	0.0088 a	0.0066 a	0.0071
	plant	2.04	1.77	2.21	2.40 a	2.21 b	1.37 ab
Cd	water	0.0017	0.0023	0.0022	0.0023 a	0.0018 ab	0.0024 b
	plant	0.79	0.83 a	0.47 a	0.79	0.73	0.74

VII: *Statistically significant differences between the subsequent years of the study*

Parameter		Year	
		2012 N=128	2013 N=128
pH		7.14*	7.00*
Electrolytic conductivity		2046.45	1954.40
Cu	water	0.0036 *	0.0101*
	plant	5.56	4.65
Ni	water	0.0030*	0.0118 *
	plant	1.91	1.87
Cd	water	0.0010*	0.0034*
	plant	0.47*	1.03*

* differences significant statistically at $p < 0.05$

VIII: *Correlation coefficients*

	Cu water	Cu plant	Ni water	Ni plant	Cd water	Cd plant	pH
Cu water	1.0000						
Cu plant	–0.0164	1.0000					
Ni water	0.7128	–0.1295	1.0000				
Ni plant	0.0761	0.4909	–0.0322	1.0000			
Cd water	0.6953	–0.0646	0.5833	0.0475	1.0000		
Cd plant	0.3938	0.1969	0.3459	0.0785	0.3484	1.0000	
pH	–0.0423	–0.1138	–0.2166	0.0021	0.1788	–0.2215	1.0000
Conductivity	0.0689	–0.0913	–0.0226	–0.1890	0.0949	–0.0886	0.5972

IX: *Statistically significant differences (p < 0.05) between the nature of catchments for its various kinds and particular examined parameters (Kruskal-Wallis test)*

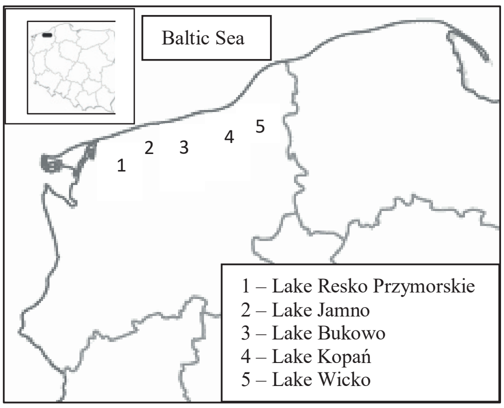
Conductivity	P	MA	A	pH	P	MA	A
STP	0.2260	0.0002	0.0000	STP	0.0091	1.0000	0.0027
P		0.0000	0.0000	P		0.0010	1.0000
MA			0.0000	MA			0.0004
Cd plant	P	MA	A	Cd water	P	MA	A
STP	0.0034	1.0000	1.0000	STP	1.0000	0.1222	0.1814
P		0.1427	0.0294	P		0.7852	0.5849
MA			1.0000	MA			1.0000
Ni plant	P	MA	A	Ni water	P	MA	A
STP	1.0000	0.6577	0.0395	STP	1.0000	0.0000	1.0000
P		0.2292	0.0147	P		0.0088	1.0000
MA			0.6989	MA			0.0679
Cu plant	P	MA	A	Cu water	P	MA	A
STP	0.0101	1.0000	0.5943	STP	0.1693	0.0000	0.0159
P		0.1413	1.0000	P		0.0002	1.0000
MA			1.0000	MA			0.3961

*P value for multiple comparisons (bilateral))
*Independent variable (grouping): Type of area. Kruskal-Wallis test
*Differences significant statistically are marked in red (p < 0.05)
*STP – area in vicinity of sewage treatment plant; P – area without additional sources of pollution; MA – area in vicinity of milibary airport; A – area affected by an intense agriculture

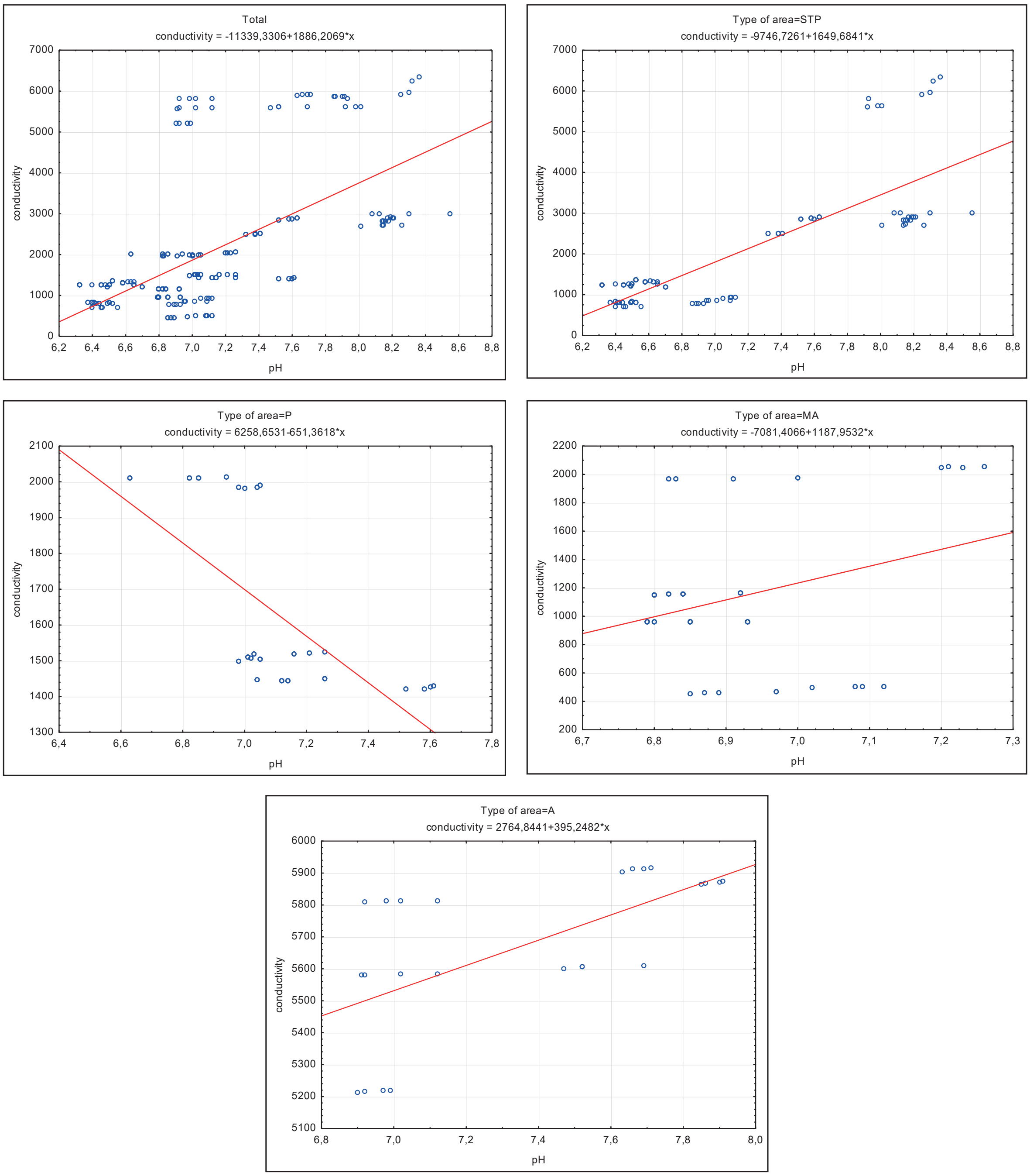
X: *Relationship between metals content in the plants and water pH*

	2	3	pH	2	3
1	0.0008	0.0000	**1**	0.0000	0.0000
2		0.0000	**2**		0.0000
Cd plant	2	3	**Cd water**	2	3
1	1.0000	0.0513	**1**	1.0000	0.8061
2		0.0000	**2**		0.4644
Ni plant	2	3	**Ni water**	2	3
1	1.0000	0.4799	**1**	0.0078	0.0000
2		0.9187	**2**		0.0219
Cu plant	2	3	**Cu water**	2	3
1	0.0873	1.0000	**1**	0.0001	0.0001
2		0.0201	**2**		1.0000

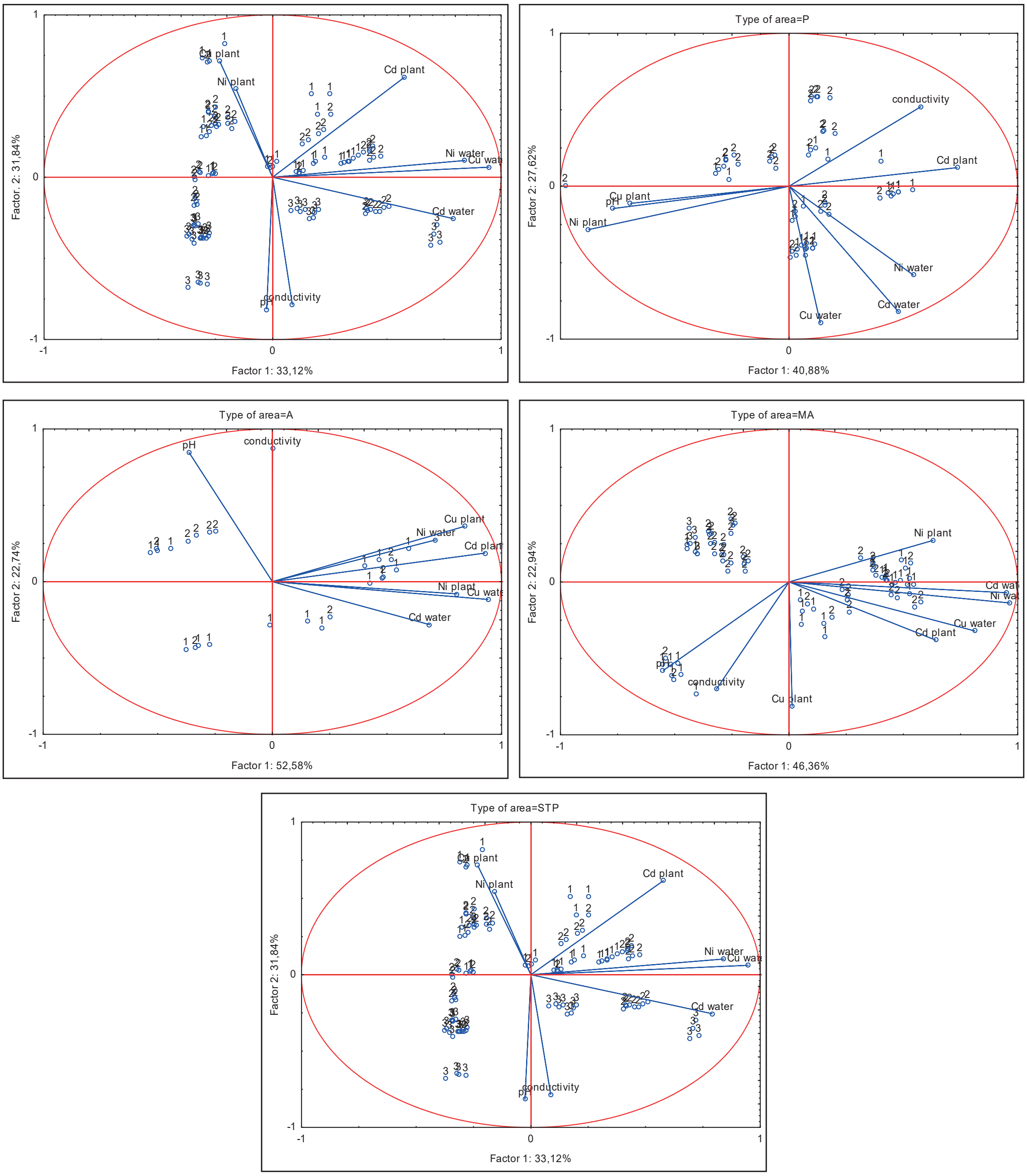
* P value for multiple comparisons (bilateral), * Independent variable (grouping): waterpH. Kruskal-Wallis test, * Differences significant statistically are marked in red (p < 0.05)



1: *Study area and location of the study lakes*



2: *Diagrams of reaction dispersion with respect to electrolytic conductivity for all data in total and with respect to the nature of the catchment.* STP – area in vicinity of sewage treatment plant, P – area without additional sources of pollution, MA – area in vicinity of military airport, A – area affected by an intense agriculture



3: *Ordination of the study sites by PCCA for All data in Total and depending on the nature of the catchment, depending on water pH.*
STP – area in vicinity of sewage treatment plant, P – area without additional sources of pollution, MA – area in vicinity of military airport, A – area affected by an intense agriculture
1 – below 6.5;
2 – 6.51–7.5;
3 – above 7.5

CONCLUSION

- The metal with the lowest concentrations in the water was cadmium, while the highest – nickel or copper, depending on the year: Cd < Ni < Cu (in 2012) and Cd < Cu < Ni (in 2013).
- In second year of the study all concentration of metals were higher than in first year. The reason could be rains which are noted in 2013 in the lake basin. Metals could be remove for example from soils. In the same time content of metals in plants were similar in both of years.
- The metal with the lowest content in the plants, like in the water, was cadmium, and the concentrations of all the three metals can be arranged as follows in the both years: Cd < Ni < Cu.
- The metal contents and metal bio-accumulation in hydro-macrophytes, expressed by means of the bio-accumulation factor (BCF), can be presented as: Cd < Ni < Cu.
- The metal bio-accumulation in *Phragmites australis*, which presence was detected in each lake, was as follows: it was the lowest for copper and cadmium in Lake Bukowo, and the highest in Lake Kopań (Bukowo < Wicko < Resko Przymorskie < Jamno < Kopań); the lowest for nickel in Lake Resko Przymorskie, and the highest in Lake Bukowo (Resko Przymorskie < Jamno < Wicko < Kopań < Bukowo).
- Examined parameters significantly depended (except Cd content in water) on catchment nature.
- Alkaline reaction of water affected the content of Cu and Cd in the examined plants.

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