Possibility of Metal Accumulation in Reed Canary Grass (Phalaris arundinacea L.) in the Aquatic Environment of South-Western Polish Rivers

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Abstract: A four-year research study was conducted on aquatic plants (reed canary grass) growing in the beds of three rivers and their tributaries in Lower Silesia, Poland. Metal contents (Cu, Cd, Ni, Pb, Zn, Fe, Mn) were determined in plant samples, metal accumulation in water (BCFw) and sediment (BCFS), Metal Pollution Index (MPI) and Enrichment Factor (EF) were calculated. The highest contents of copper, lead, nickel and cadmium were found in reed canary grass sampled from the Nysa Szalona River. The highest values were recorded for zinc in the Bystrzyca River, and for iron and manganese in the Strzegomka River. The series of metals were as follows: Nysa Szalona and Strzegomka: Cd < Ni < Pb < Cu < Zn < Mn < Fe, Bystrzyca: Cd < Ni < Cu < Pb < Zn < Mn < Fe. Throughout the study period, the lowest values of metals in plants were recorded in 2015 and 2018, and the highest in 2017. The general picture of MPI in aquatic plants is arranged in the series Bystrzyca < Strzegomka < Nysa Szalona. These values classify the studied material at a high level of pollution in all rivers. In the comparison of the two extreme sites, i.e., source-mouth, higher values were found at the mouth of the reservoir, which suggests that metals move with the water current and accumulate more with the direction of the river flow, which is most likely a consequence of the influence of the catchment area as the source of metals. The series of EF enrichment factor values were as follows: Bystrzyca—Ni < Cd < Fe < Cu < Zn < Mn < Pb, Nysa Szalona—Ni < Fe < Zn < Cd < Mn < Cu < Pb, Strzegomka—Ni < Cd < Fe < Zn < Cu < Pb < Mn. For all the samples studied, the values found in spring were much higher than in autumn, which indicates the great importance for research in that area. The levels of copper and iron were within the range of moderate values, lead and manganese reached very high and exceptionally high values, and the remaining metals were within the values described as significant. Bioaccumulation of metals determined relative to bottom sediments was highest in 2017 and lowest in 2018, while bioaccumulation relative to water was highest in 2018 and lowest in 2016. The four-year study found that the metal content in reed canary grass was mostly within the range of mean values presented in the literature from moderately polluted areas. Also, no significant deviation was found from levels that have been recorded for the same rivers for more than two decades.

Keywords: aquatic plants; copper; cadmium; lead; nickel; zinc; iron; manganese

1. Introduction

Natural levels of metals in the environment are disrupted by industrial, agricultural and municipal activities. Each type of activity often results in a different metal load to the air, soil, groundwater and surface water. Elevated levels of some metals are not the cause of significant changes in the environment and do not have a strong toxic effect...
on its components. However, there is a group of metals, the presence of which even
at low concentrations can cause deterioration in the quality of the environment. All of
the environmental components have an effect on human life, but some of them, such as
waters being a source of drinking supply, should be under special supervision. Apart from
groundwater reservoirs, this type of water includes surface waters—lakes and rivers as well
as dam reservoirs built on them. They are supplied by river waters and accumulate material
originating from catchment areas. The main rivers and their tributaries carry characteristic
pollutants collected in the catchment. As a rule, in mountain catchments, in contrast to
lowland catchments, the material is poorer in organic components and the components
carried with the faster current have limited possibilities of being deposited in the form of
bottom sediment. This can result in a reduced amount of available rooting sites for aquatic
plants, and free-floating macrophytes are unlikely to find a place for themselves due to
the rapid water flow. An additional factor depleting the number of plants in mountain
riverbeds is their transformation by humans. This is associated with the ongoing regulation
of rivers, which entails the concreting of their beds and banks, thus eliminating potential
habitats for plant rooting, as well as reducing the species composition and abundance of
organisms. As a consequence, the number of aquatic organisms treated as pollutant filterers
carrying water from the catchment is reduced. Such activities are important from the point
of view of using water for domestic purposes and as drinking water [1–5].

The amount of organic and mineral compounds carried with river waters is a result
not only of natural but also anthropogenic activities. It may also be a further consequence of
specific conditions for the release of metals from soil and sediments, which under favorable
circumstances, e.g., excessive acidification, become more mobile and available for uptake
by plants. The mobility of elements depends, among others, on the reaction of water.
This is the case of metals, which become a threat to the state of water quality in a more
strongly acidified or alkalized environment [6–10]. The presence of metals in aquatic plants
is also related to their level in the atmospheric air. In the areas burdened by a stronger
anthropogenic influence and subjected to natural activities of this character, their level in the
air is higher, which is reflected in the chemical composition of soil and water, and further on
in macrophytes. More than 90% of cadmium, copper, mercury, lead and zinc compounds in
bottom sediments have their source in anthropogenic industrial pollution. Table 1 presents
average the metal contents in particular components of the natural environment [11,12].
These elements belong to the group of trace, cyclic elements occurring most numerously in
nature, constituting 99.9% of the mass of the Earth’s crust and playing a significant role
in the environment. Their characteristic feature is the ability to react and repeatedly form
the same compounds. In addition, manganese, iron and copper are defined as biophilic
elements, as those which are part of living organisms and their circulation is largely related
to the course of biological processes. As a rule, the natural circulation of elements takes
place in a balanced way, but when anthropogenic activity becomes a stimulus, this order
may be disturbed. It is visible in the process of accumulation of metals, among which there
are groups more (Cu, Cd, Pb, Zn) or less susceptible to accumulation (Fe, Mn). All of these
elements, in larger quantities, pose a threat to the environment, which can transform from
a local impact into a threat of a wider scope. In the case of aquatic plants, susceptibility to
bioaccumulation from water concerns mainly cadmium, lead, copper and zinc, and from
bottom sediment—cadmium and zinc [12].

In the south-western part of Poland, where rivers and reservoirs are the main stores of
drinking water, the study included three rivers: Nysa Szalona, Bystrzyca and Strzegomka,
supplying the reservoirs Słup, Dobromierz and Lubachów, respectively. They differ in
structure, but mainly in their location above sea level and character: lowland, submontane
and mountainous.
Table 1. Ranges of metal content in environmental components [11,12].

| Metal/Unit | Air         | Waters       | Soils       | Plants      |
|------------|-------------|--------------|-------------|-------------|
|            | ng m\(^{-3}\) | mg dm\(^{-3}\) | mg kg\(^{-1}\) | mg kg\(^{-1}\) |
| Cu         | 0.03–4900.00 | 0.001–0.020  | 3.00–25.00  | 5.00–30.00  |
| Cd         | 0.003–0.60   | 0.00001–0.00002 | 0.0002–0.60 | 0.05–0.20   |
| Ni         | 0.10–1.00    | 0.0001–0.0075 | 5.00–22.00  | 0.10–5.00   |
| Pb         | 0.50–10.00   | 0.0002–0.0003 | 25.00–40.00 | 0.10–5.00   |
| Zn         | 0.002–0.05   | 1.00–110.00  | 10.00–220.00| 10.00–70.00 |
| Fe         | 0.50–6000.00 | 0.01–1.40    | 8000.00–18,000.00 | 50.00–200.00 |
| Mn         | 0.02–900.00  | 0.02–0.06    | 100.00–1300.00 | 70.00–500.00 |

Until now, no such comprehensive and long-term study of aquatic vegetation has been conducted within these reservoirs. Although some sections of rivers and reservoirs were included in the analysis, it was not a comprehensive study [12–16]. The authors studied water and bottom sediments simultaneously in this area [17,18]. All of these components would provide a holistic picture of the environment of these three catchments, including not only the dam reservoirs themselves, but the main rivers feeding them along with all tributaries. First of all, this study will make it possible to determine the quality of the environment from the natural point of view. Understanding the levels of metals in hydro- macrophytes is important from the point of view of plant health, but also their usefulness in cleaning the aquatic environment. Secondly, such comprehensive studies, as in this case, will make it possible to indicate potential threats to the quality of water which supply reservoirs intended for drinking water.

The aim of this study was to determine the possibility of accumulation of metals (Cu, Zn, Pb, Ni, Fe, Mn) in reed canary grass growing in rivers feeding the three reservoirs. Water from the reservoirs is taken as drinking water, so testing for water pollution and biotic elements is advisable. Reed canary grass is a plant that grows in all the beds of these rivers and may, in this situation, be used as an indicator plant.

2. Materials and Methods

2.1. Study Area

The study covered the following areas in south-west Poland: N 50°38’10.1652”–N 51°4’31.7745” and E 16°3’54.4715”–E 16°25’1.4097” [19,20]. The study included three Lower Silesian rivers: Nysa Szalona, Strzegomka and Bystrzyca along with their tributaries from the sources to their mouths in the dam reservoirs Slup, Dobromierz and Lubachów (Figure 1; Tables 2–4).

Table 2. Research sites—the Nysa Szalona River and its tributaries above the Slup dam reservoir [19].

| No | Site—Geographical Coordinates | Surface Water Types, Water Categories—Type Code SWB * Status |
|----|--------------------------------|------------------------------------------------------------|
| 1  | The Nysa Szalona River below the springs in Domanów—N 50°51’38.8261” E 16°3’54.4715” | Upland silicate stream with coarse-grained substrate—western natural |
| 2  | Kocik—N 50°52’15.4891” E 16°4’5.9042” |
| 3  | Ochodnik—E 16°3’55.79.7672” |
| 4  | Sadówka—N 50°55’58.609” E 16°10’11.3627” |
| 5  | Czyścieł—N 50°57’49.4252” E 16°13’57.6982” |
| 6  | Radynia—N 50°58’56.648” E 16°14’13.9202” |
Table 2. Cont.

| No | Site—Geographical Coordinates | Surface Water Types, Water Categories—Type Code |
|----|--------------------------------|-----------------------------------------------|
|    |                               | SWB * Status                                   |
| 7  | Nysa Mała—N 51°0’10.455″ E 16°12’26.0825″ | Upland carbonate stream with coarse-grained substrate 7 natural |
| 8  | Puszówka—N 51°2’30.3945″ E 16°11’39.425″  | Upland silicate stream with fine-grained substrate—western 5 natural |
| 9  | Jawornik—N 51°2’57.6884″ E 16°10’52.4584″  |                                             |
| 10 | Księginka—N 51°3’17.4033″ E 16°10’11.2082″ |                                             |
| 11 | Starucha—N 51°4’31.7745″ E 16°6’17.7528″   |                                             |
| 12 | Rowiec—N 51°4’22.844″ E 16°8’27.5419″       |                                             |
| 13 | Męcinka—N 51°4’29.2507″ E 16°7’28.5247″     |                                             |
| 14 | Nysa Szalona mouth to the Słup reservoir—N 51°4’29.2507″ E 16°7’28.5247″ | Small upland silicate river—western 8 artificial watercourse |

* SWB—surface water body.

Figure 1. Location of the study area, 1—Słup reservoir—research sites on the Nysa Szalona River and its tributaries (Table 2), 2—Dobromierz reservoir—research sites on the Strzegomka River and its tributaries (Table 3), 3—Lubachów reservoir—research sites on the Bystrzyca River and its tributaries (Table 4).
Table 3. Research sites—the Strzegomka River and its tributaries above the Dobromierz dam reservoir [19].

| No | Site—Geographical Coordinates | Surface Water Types, Water Categories—Type Code SWB * Status |
|----|--------------------------------|----------------------------------------------------------|
| 1  | The Strzegomka River below the springs in Nowe Bogaczowice—N 50°50'14.5978" E 16°7'49.8450" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 2  | Polska Woda—N 50°52'48.0601" E 16°11'56.4194" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 3  | Sikorka—N 50°51'47.2613" E 16°13'21.3918" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 4  | Czyżynka—N 50°52'15.8303" E 16°14'29.8332" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 5  | Strzegomka mouth to the Dobromierz reservoir—N 50°53'11.1994" E 16°13'58.4707" | Upland silicate stream with coarse-grained substrate—western 4 artificial |

* SWB—surface water body.

Table 4. Research sites—the Bystrzyca River and its tributaries above the Lubachów dam reservoir [19].

| No | Site—Geographical Coordinates | Surface Water Types, Water Categories—Type Code SWB * Status |
|----|--------------------------------|----------------------------------------------------------|
| 1  | The Bystrzyca River below the springs in Wrześni—N 50°38'10.1652" E 16°24'5.7915" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 2  | Złoty Potok—N 50°38'29.3697" E 16°24'1.0163" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 3  | Kłobia—N 50°40'9.3747" E 16°23'27.0131" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 4  | Ołuczyna—N 50°40'36.2015" E 16°22'46.8444" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 5  | Potok Marowy Duży—N 50°41'5.2762" E 16°22'32.3218" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 6  | Złota Woda—N 50°41'4.2973" E 16°22'11.0015" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 7  | Rybnica—N 50°41'49.8085" E 16°21'58.1784" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 8  | Jaworzynka—N 50°43'25.8799" E 16°23'56.5218" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 9  | Walimianka—N 50°43'49.9381" E 16°24'15.0612" | Upland silicate stream with coarse-grained substrate—western 4 artificial |
| 10 | Bystrzyca mouth to the Lubachów reservoir—N 50°45'5.8065" E 16°25'1.4097" | Upland silicate stream with coarse-grained substrate—western 4 artificial |

* SWB—surface water body.

The characteristics of the rivers under examination are presented in Table S1 [13–15,19,20].

2.2. Material

Reed canary grass (*Phalaris arundinacea* L.) was sampled twice a year at the beginning (May) and at the end of the growing season (October). The study was conducted from 2015 to 2018. Plants were collected from main rivers, and additionally from tributaries at a distance of 50 m before their mouths (Figure 1, Tables 2–4) [21–23].

Monocotyledonous emergent plants (helophytes) were sampled. Taxonomic position of the collected plants is as follows:

Domain: *Eucaryota*—eukaryotes

Kingdom: *Archaeplastida* (*Plantae*)—plants

Clade: *Spermatophyta*—spermatophytes

Class: *Liliopsida* (*Monocotyledones*)—monocotyledons

Order: *Poales* (*Graminales*)—Glumiflorae

Family: *Poeceae* (*Gramineae*)—grasses

Subfamily: *Pooideae*

Tribe: *Poeae*
Subtribe: Phalaridinae
Species: reed canary grass (*Phalaris arundinacea* L.)

Reed canary grass was harvested whole (root, stem, leaves, and inflorescence). Immediately at the test site after collection, plants were washed with river water. In the laboratory, they were dried at room temperature to an air-dry state and then cut, crushed, and homogenized.

For the determination of metals, 0.5 g of air-dry and homogenized sample was weighed in an HP-500 Teflon dish. Then, 10 cm$^3$ of concentrated HNO$_3$ (Sigma-Aldrich, Poznań, Poland) was added and the samples were left at room temperature for 24 h. After this time, the samples were placed in a Mars 5 microwave oven (CEM) and mineralized using a 3-stage mineralization. After cooling to room temperature, the mineralizates were transferred to test tubes and diluted with distilled water to 25 cm$^3$ [24–26].

232 plant samples were collected and results are given in mg·kg$^{-1}$ dry weight.

The levels of lead, copper, nickel, zinc, cadmium, iron and manganese in aquatic plants were determined by flame atomic absorption spectrometry (FAAS) using a Spectra AA-110/220 from Varian [27].

Test results were verified using certified reference materials for aquatic plants—IAEA-336 International Atomic Energy Agency—Analytical Quality Control Services Austria and CRM 482—Commission of the European Communities, Community Bureau of Reference—BCR.

Accumulation of metals in aquatic plants was determined by:

- metals bioaccumulation factor (BCF$_B$) as a ratio of its content in aquatic plant ($C_P$) to its concentration in bottom sediment ($C_B$) [28]

$$BCF_B = \frac{C_P}{C_B}$$

- metals bioaccumulation factor BCF$_W$ as a ratio of its content in aquatic plant $C_P$ to its concentration in water $C_W$ [28]

$$BCF_W = \frac{C_P}{C_W}$$

The assessment of the state of plants contamination with metals was carried out using the metal pollution index (MPI) [29].

$$MPI = (Cf_1 \times Cf_2 \ldots Cf_n)^{1/n}$$

where $Cf_1$, $Cf_2$ . . . $Cf_n$—concentration of first metal, second metal, $n$-th metal.

MPI values less than 2 indicate no impact on pollution degree, values 2–5—very low impact, 5–10 low impact, 10–20 medium impact, 20–50 high impact, 50–100 very high impact, above 100 the highest impact.

The metal contamination status of aquatic plants was also assessed using the metal enrichment factor (EF) [30].

$$EF = (Me/Al)_{\text{sample}}/(Me/Al)_{\text{background}}$$

$Me$—particular metal, $Al$—aluminum.

For individual metals, the following values were taken as background: Al—1708; Cd—1.03; Cu—4.95; Zn—40; Pb—1.45; Mn—115; Fe—210; Ni—9.51 [12].

EF values less than 2 indicate no or minimal enrichment of the plant with particular metals, range 2–5 as moderate, 5–20 as significant, 20–40 as very high, and above 40 as extremely high [30].
2.3. Statistical Analysis

The analysis of results was performed using Microsoft Office Excel 2019 and Statistica 13.0 (StatSoft Poland, Krakow, Poland). Calculations were performed using R version 3.6.0. The Shapiro-Wilk test was applied to check the normality of the distribution. Spearman correlations were used due to the distribution of samples. Spearman correlations were calculated in Statistica, and box and whisker plots were also created in this program. All statistically significant differences were calculated at \( p < 0.05 \). Because the data had a non-normal distribution, the Kruskal-Wallis test with post-hoc analysis was used. A PCA test using the r-groups statistic (RStudio Version 1.1.442-© 2022–2018, Rstudio, Inc., Boston, MA, USA) was used to visualize differences between groups. It was based on all data and presented the differences in the parameters of the studied plant depending on the year, season of study and river.

3. Results and discussion

3.1. Metals in Reed Canary Grass

The highest contents of Cu, Ni, Cd, Pb were recorded in reed canary grass sampled from the Nysa Szalona River (Table 5). Samples from the Bystrzyca River had the highest zinc levels, while samples from the Strzegomka River had the highest iron and manganese levels. The lowest values of Fe, Mn and Zn were recorded in plants obtained from the Nysa Szalona River, Pb and Cd from the Strzegomka River, and Cu and Ni from the Bystrzyca River. The series of metals were as follows: Nysa Szalona and Strzegomka: Cd < Ni < Pb < Cu < Zn < Mn < Fe, and Bystrzyca: Cd < Ni < Cu < Pb < Zn < Mn < Fe.

Table 5. Metal content (mg kg\(^{-1}\)) of reed canary grass in three main rivers and their tributaries over a four-year study cycle.

| Metal | River | Index  | 2015            | 2016            | 2017            | 2018            | Min–Max     |
|-------|-------|--------|-----------------|-----------------|-----------------|-----------------|-------------|
|       |       |        |                | Min–Max         | \( \bar{x} \pm SD \) |                |             |
|       |       | P      | 3.69–396.55     | 4.96–19.74      | 2.33–20.98      | 3.44–27.89      | 31.02 ± 63.63|
|       |       |        | 92.79 ± 105.07  | 9.40 ± 2.99     | 10.85 ± 4.90    | 11.04 ± 5.80    |             |
|       | NS    | BCF\(_B\) | 0.0090–13.13    | 0.0190–0.5860   | 0.0596–2.12     | 0.1037–1.58     | 1.11 ± 2.14  |
|       |       |        | 2.92 ± 3.63     | 0.1550 ± 0.15   | 0.8538 ± 0.58   | 0.5280 ± 0.34   |             |
| Cu    |       |        | 1923.00–82,142.29 | 56.26–232.98   | 664.66–5878.06 | 40.60–2045.71  | 319.32 ± 373.18|
|       |       | BCF\(_W\) | 19,842.46 ± 23,950.61 | 134.06 ± 46.13 | 2637.96 ± 1622.71 | 319.32 ± 373.18|
|       |       |        | 5733.45 ± 14,540.62 |                |                |                |             |
|       |       | P      | 3.36–15.89      | 3.96–9.00       | 2.89–23.78      | 3.45–13.47      | 7.92 ± 3.78  |
|       |       |        | 8.15 ± 2.95     | 6.66 ± 1.30     | 10.09 ± 5.83    | 6.76 ± 2.26     |             |
| B     |       | BCF\(_B\) | 0.0154–2.77     | 0.0107–1.14     | 0.2479–2.97     | 0.0982–1.63     | 0.5545 ± 0.55|
|       |       |        | 0.4269 ± 0.59   | 0.3214 ± 0.29   | 0.8282 ± 0.66   | 0.6413 ± 0.42   |             |
|       |       | BCF\(_W\) | 437.38–15,894.30 | 919.94–5736.77 | 484.54–4634.65 | 32.31–247.52   | 2066.48 ± 2126.21|
Table 5. Cont.

| Metal | River | Index | 2015        | 2016        | 2017        | 2018        |
|-------|-------|-------|-------------|-------------|-------------|-------------|
|       |       |       | Min–Max     | Min–Max     | Min–Max     | Min–Max     |
|       |       |       | x ± SD      | x ± SD      | x ± SD      | x ± SD      |
| Cu    | S     | P     | 9.41–13.98  | 8.07–29.89  | 9.34–22.68  | 3.02–7.93   |
|       |       | 11.74 ± 1.31 | 16.47 ± 7.26 | 13.59 ± 3.55 | 5.75 ± 1.58 |
|       |       |       | 11.89 ± 5.72 |            |             |             |
|       |       | BCFB  | 0.6326–1.99 | 0.6109–4.25 | 0.9014–2.24 | 0.2281–1.11 |
|       |       |       | 1.24 ± 0.38 | 1.57 ± 1.00 | 1.32 ± 0.37 | 0.5561 ± 0.26 |
|       |       |       | 1.17 ± 0.69 |            |             |             |
|       |       | BCFW  | 1300.77–5589.87 | 1832.68–4519.43 | 1355.33–9448.13 | 30.47–157.37 |
|       |       |       | 2385.15 ± 1255.77 | 3133.91 ± 904.62 | 3102.78 ± 2409.48 | 86.93 ± 44.08 |
|       |       |       | 2177.04 ± 1896.46 |            |             |             |
|       |       | P     | 0.5964–9.87 | 0.5632–1.96 | 0.4512–1.83 | 0.5612–1.13 |
|       |       |       | 3.64 ± 3.05 | 0.99 ± 0.26 | 1.07 ± 0.29 | 0.8932 ± 0.16 |
|       |       |       | 1.65 ± 1.92 |            |             |             |
|       |       | BCFB  | 0.1021–21.78 | 0.1091–7.85 | 0.4114–2.4820 | 0.4733–41.07 |
|       |       |       | 4.95 ± 5.92 | 1.02 ± 1.45 | 1.11 ± 0.44 | 1.21 ± 4.37 |
|       |       |       | 2.09 ± 4.10 |            |             |             |
|       |       | BCFW  | 504.68–10,256.00 | 265.50–9652.00 | 760.50–15,345.00 | 13.96–1447.43 |
|       |       |       | 3665.21 ± 2645.85 | 1602.14 ± 1800.53 | 3877.44 ± 3409.34 | 70.79 ± 242.36 |
|       |       |       | 2303.89 ± 2816.61 |            |             |             |
|       |       | P     | 0.22–1.24 | 0.6312–10.89 | 0.4512–1.83 | 0.5612–1.13 |
|       |       |       | 0.76 ± 0.30 | 1.09 ± 1.28 | 1.31 ± 0.31 | 0.45 ± 0.57 |
|       |       |       | 0.9046 ± 0.80 |            |             |             |
| Cd    | B     | BCFB  | 0.2575–4.09 | 0.2020–10.86 | 0.6409–3.24 | 0.0209–2.20 |
|       |       |       | 0.9804 ± 0.86 | 1.60 ± 1.70 | 1.67 ± 0.74 | 0.50 ± 0.57 |
|       |       |       | 1.1860 ± 1.17 |            |             |             |
|       |       | BCFW  | 35.85–12,389.00 | 1308.33–18,155.50 | 1244.57–16,091.00 | 71.40–12,385.00 |
|       |       |       | 2785.70 ± 2956.48 | 4291.59 ± 3190.04 | 6401.30 ± 5395.53 | 1626.52 ± 2633.81 |
|       |       |       | 3776.28 ± 4114.76 |            |             |             |
|       |       | P     | 0.74–1.16 | 0.7412–1.25 | 0.1111–2.08 | 0.1111–1.45 |
|       |       |       | 0.92 ± 0.12 | 0.93 ± 0.13 | 1.05 ± 0.52 | 0.69 ± 0.39 |
|       |       |       | 0.8969 ± 0.36 |            |             |             |
|       |       | BCFB  | 0.8831–1.71 | 0.8567–2.21 | 0.1297–2.99 | 0.1297–1.68 |
|       |       |       | 1.25 ± 0.25 | 1.44 ± 0.37 | 1.59 ± 0.92 | 0.7913 ± 0.45 |
|       |       |       | 1.27 ± 0.63 |            |             |             |
|       |       | BCFW  | 534.06–8644.00 | 828.58–7532.00 | 185.17–17,076.00 | 5.35–44.55 |
|       |       |       | 1909.34 ± 2268.10 | 2320.29 ± 1560.09 | 2870.36 ± 4765.91 | 18.16 ± 9.89 |
|       |       |       | 1779.54 ± 2953.55 |            |             |             |
Table 5. Cont.

| Metal | River | Index | 2015       | 2016       | 2017       | 2018       |
|-------|-------|-------|------------|------------|------------|------------|
|       |       |       | Min–Max    | Min–Max    | Min–Max    | Min–Max    |
|       |       |       | Max        | Max        | Max        | Max        |
|       |       |       | μ ± SD     | μ ± SD     | μ ± SD     | μ ± SD     |
| Ni    | P     |       | 0.2654–15.66 | 3.25–9.35  | 3.34–18.44 | 1.72–14.84 |
|       |       |       | 5.46 ± 5.33 | 6.46 ± 1.62 | 7.98 ± 3.22 | 7.15 ± 3.18 |
|       |       |       | 6.76 ± 3.71 |            |            |            |
|       | NS    | BCF_B | 0.0061–0.0787 | 0.0059–0.3128 | 0.0663–0.8549 | 0.0212–0.5079 |
|       |       |       | 0.0233 ± 0.01 | 0.1006 ± 0.10 | 0.2922 ± 0.17 | 0.1891 ± 0.11 |
|       |       |       | 0.1513 ± 0.15 |            |            |            |
|       | BCF_W |       | 63.16–13,014.50 | 21.91–200.52 | 146.06–5273.90 | 12.74–943.87 |
|       |       |       | 4904.16 ± 4274.31 | 86.29 ± 45.55 | 1740.10 ± 868.51 | 100.54 ± 185.67 |
|       |       |       | 1707.77 ± 2936.45 |            |            |            |
|       | Ni    | BCF_B | 1.63–8.27 | 3.34–9.46 | 3.73–13.98 | 0.1625–4.35 |
|       |       |       | 4.38 ± 1.95 | 6.22 ± 1.60 | 8.09 ± 3.11 | 1.81 ± 1.54 |
|       |       |       | 5.12 ± 3.16 |            |            |            |
|       | BCF_W |       | 0.0061–1.12 | 0.0187–0.9039 | 0.1189–1.03 | 0.0041–0.3889 |
|       |       |       | 0.2746 ± 0.31 | 0.3287 ± 0.27 | 0.4492 ± 0.23 | 0.1081 ± 0.10 |
|       |       |       | 0.2900 ± 0.27 |            |            |            |
|       |       |       | 1088.07–8872.25 | 2224.60–7880.50 | 199.35–3233.07 | 0.7329–42.14 |
|       |       |       | 4070.95 ± 2000.95 | 3777.76 ± 1349.49 | 1870.45 ± 765.77 | 16.66 ± 14.51 |
|       |       |       | 2408.95 ± 2049.19 |            |            |            |
|       | Pb    | BCF_B | 4.42–9.07 | 2.95–8.49 | 4.37–31.67 | 2.88–6.91 |
|       |       |       | 6.11 ± 1.26 | 5.29 ± 1.63 | 10.85 ± 7.58 | 4.16 ± 1.06 |
|       |       |       | 6.60 ± 4.71 |            |            |            |
|       |       | BCF_W | 0.2072–0.3550 | 0.1305–0.3908 | 0.2241–1.57 | 0.1356–0.3515 |
|       |       |       | 0.2884 ± 0.05 | 0.2518 ± 0.08 | 0.5080 ± 0.37 | 0.1990 ± 0.06 |
|       |       |       | 0.3111 ± 0.23 |            |            |            |
|       |       |       | 28.32–2108.77 | 717.68–2178.60 | 30.77–7256.98 | 15.35–51.48 |
|       |       |       | 700.64 ± 709.76 | 1311.65 ± 364.22 | 1648.45 ± 2182.31 | 29.99 ± 8.54 |
|       |       |       | 922.69 ± 1315.60 |            |            |            |
|       | Pb    | BCF_B | 13.00–87.36 | 10.43–29.88 | 6.02–38.65 | 1.73–47.55 |
|       |       |       | 36.82 ± 18.85 | 16.65 ± 4.04 | 16.82 ± 7.75 | 18.74 ± 13.53 |
|       |       |       | 22.26 ± 15.00 |            |            |            |
|       |       | BCF_W | 0.0513–2.76 | 0.0185–8.832 | 0.1039–3.79 | 0.1027–1.86 |
|       |       |       | 0.6813 ± 0.75 | 0.3040 ± 0.26 | 0.9058 ± 0.89 | 0.7196 ± 0.45 |
|       |       |       | 0.6527 ± 0.6734 |            |            |            |
|       |       |       | 245.43–56,963.20 | 3257.25–8316.06 | 2153.48–48,141.50 | 6.03–8807.83 |
|       |       |       | 15,757.36 ± 15,294.00 | 5692.71 ± 1346.02 | 14,263.33 ± 9914.17 | 362.88 ± 1528.85 |
|       |       |       | 9019.07 ± 11,127.08 |            |            |            |
| Metal | River | Index  | 2015   | 2016   | 2017   | 2018   |
|-------|-------|--------|--------|--------|--------|--------|
|       |       |        | Min–Max |        |        |        |
|       |       |        | τ ± SD  |        |        |        |
| Pb    |       | P      | 2.41–16.07 | 17.43–42.85 | 8.45–28.95 | 1.63–11.51 |
|       |       |        | 5.91 ± 3.24 | 25.71 ± 6.98 | 17.57 ± 5.60 | 6.29 ± 2.84 |
|       |       |        | 13.87 ± 9.72 |        |        |        |
|       |       | BCF<sub>B</sub> | 0.0013–0.2969 | 0.0099–0.8208 | 0.0736–0.5899 | 0.0102–0.1984 |
|       |       |        | 0.0645 ± 0.07 | 0.2841 ± 0.24 | 0.3056 ± 0.14 | 0.0988 ± 0.05 |
|       |       |        | 0.1880 ± 0.18 |        |        |        |
|       |       | BCF<sub>W</sub> | 471.17–38,613.00 | 7812.33–24,963.20 | 2224.36–219,934.00 | 549.78–7290.42 |
|       |       |        | 5535.71 ± 7137.87 | 18,932.01 ± 3872.30 | 21,749.61 ± 39,393.70 | 2811.04 ± 1588.59 |
|       |       |        | 12,212.09 ± 21,747.66 |        |        |        |
|       |       | S      | 4.37–12.05 | 5.13–14.65 | 5.63–15.98 | 3.91–10.94 |
|       |       |        | 7.64 ± 2.08 | 9.02 ± 2.66 | 10.26 ± 3.03 | 8.02 ± 1.81 |
|       |       |        | 8.74 ± 2.64 |        |        |        |
|       |       | BCF<sub>B</sub> | 0.0457–0.3607 | 0.0515–0.2591 | 0.0843–0.4159 | 0.0618–0.2174 |
|       |       |        | 0.1495 ± 0.08 | 0.1313 ± 0.06 | 0.1948 ± 0.1056 | 0.1121 ± 0.04 |
|       |       |        | 0.1512 ± 0.08 |        |        |        |
|       |       | BCF<sub>W</sub> | 1213.83–11,348.50 | 2052.88–12,733.14 | 2157.64–25,128.60 | 11.34–78.23 |
|       |       |        | 3983.48 ± 2733.79 | 5682.49 ± 3019.55 | 6934.89 ± 6275.36 | 34.89 ± 14.68 |
|       |       |        | 4158.93 ± 4556.24 |        |        |        |
|       |       | NS     | 5.96–66.87 | 22.03–70.01 | 25.68–128.72 | 15.09–69.74 |
|       |       |        | 33.04 ± 18.70 | 44.32 ± 13.06 | 64.09 ± 28.20 | 35.91 ± 13.79 |
|       |       |        | 44.54 ± 23.06 |        |        |        |
|       |       | BCF<sub>B</sub> | 0.0099–0.9874 | 0.0142–0.9100 | 0.2652–3.1315 | 0.0632–0.9774 |
|       |       |        | 0.1400 ± 0.18 | 0.2511 ± 0.25 | 1.2300 ± 0.75 | 0.4465 ± 0.23 |
|       |       |        | 0.5212 ± 0.60 |        |        |        |
|       |       | BCF<sub>W</sub> | 207.77–4399.61 | 102.25–5303.62 | 420.79–14,967.59 | 13.84–2398.60 |
|       |       |        | 1792.75 ± 1358.27 | 1814.21 ± 1748.98 | 4391.97 ± 2962.07 | 246.62 ± 424.87 |
|       |       |        | 2061.39 ± 2383.09 |        |        |        |
|       |       | Zn     | 16.89–120.04 | 46.43–169.49 | 27.22–134.79 | 25.63–80.80 |
|       |       |        | 49.67 ± 23.52 | 110.38 ± 34.88 | 79.20 ± 32.27 | 47.46 ± 15.14 |
|       |       |        | 714.68 ± 37.63 |        |        |        |
|       |       | BCF<sub>B</sub> | 0.0175–2.22 | 0.0287–3.46 | 0.3857–2.77 | 0.1492–1.99 |
|       |       |        | 0.5072 ± 0.55 | 1.42 ± 1.16 | 1.37 ± 0.71 | 0.83 ± 0.47 |
|       |       |        | 1.03 ± 0.86 |        |        |        |
|       |       | BCF<sub>W</sub> | 469.27–29,163.40 | 2159.59–12,726.10 | 1645.91–6989.95 | 42.28–1513.40 |
|       |       |        | 3626.89 ± 5641.92 | 6461.84 ± 3094.85 | 3981.76 ± 1648.14 | 375.09 ± 305.49 |
|       |       |        | 3611.39 ± 3967.21 |        |        |        |
Table 5. Cont.

| Metal | River | Index | 2015          | 2016          | 2017          | 2018          |
|-------|-------|-------|---------------|---------------|---------------|---------------|
| Zn    | S     | Min–Max | 43.01–85.70   | 39.01–102.68  | 57.01–206.54  | 10.00–70.27   |
|       |       | x ± SD  | 62.17 ± 14.23 | 66.82 ± 20.11 | 104.34 ± 44.68| 34.06 ± 20.99 |
|       |       |         |               |               |               | 66.85 ± 37.24 |
|       |       | BCF_B  | 0.6694–1.78   | 0.4520–2.01   | 0.8359–3.26   | 0.1318–1.05   |
|       |       |         | 1.12 ± 0.36   | 0.9852 ± 0.46 | 1.79 ± 0.65   | 0.4766 ± 0.30 |
|       |       |         |               |               |               | 1.09 ± 0.66   |
|       |       | BCF_W  | 627.36–5909.00| 2933.10–70,158.80| 3369.96–12,008.30| 21.00–630.48 |
|       |       |         | 2432.90 ± 1845.40| 10,306.37 ± 1815.65| 6014.73 ± 2400.19| 215.14 ± 203.81|
|       |       |         |               |               |               | 4742.30 ± 9901.70 |
|       |       |         | 2.96–541.53   | 65.01–616.59  | 16.32–2946.99 | 46.44–4985.87 |
|       |       |         | 199.89 ± 204.39| 208.14 ± 123.18| 1056.19 ± 850.94| 381.03 ± 889.57|
|       |       |         |               |               |               | 461.31 ± 718.53 |
|       |       | BCF_B  | 0.0001–0.1691 | 0.0031–0.0529 | 0.0010–0.2993 | 0.0030–0.2074 |
|       |       |         | 0.0168 ± 0.02 | 0.0152 ± 0.0125| 0.0731 ± 0.0767| 0.0217 ± 0.04 |
|       |       |         |               |               |               | 0.0320 ± 0.05 |
|       |       | BCF_W  | 1.23–1694.00  | 49.48–4101.20 | 24.94–10,035.41| 29.51–2413.32 |
|       |       |         | 370.14 ± 443.67| 524.91 ± 791.51| 1754.27 ± 1980.97| 484.94 ± 529.89|
|       |       |         |               |               |               | 783.57 ± 1254.75 |
|       |       |         | 156.34–632.98 | 198.01–1002.88| 72.08–5081.90 | 87.11–695.86 |
|       |       |         | 355.48 ± 112.80| 487.69 ± 207.04| 1658.29 ± 1405.45| 331.00 ± 189.35|
|       |       |         |               |               |               | 708.12 ± 906.19 |
|       |       | BCF_B  | 0.0185–0.1030 | 0.0158–3.53   | 0.0073–0.5283 | 0.0049–2.99   |
|       |       |         | 0.0385 ± 0.02 | 0.1568 ± 0.63 | 0.1763 ± 0.16 | 0.9449 ± 1.02 |
|       |       |         |               |               |               | 0.3291 ± 0.70 |
|       |       | BCF_W  | 162.09–2758.79| 227.70–3209.08| 157.37–4535.96| 32.82–3261.00 |
|       |       |         | 360.43 ± 326.26| 564.85 ± 627.11| 1813.98 ± 1480.39| 719.64 ± 792.59|
|       |       |         |               |               |               | 864.72 ± 1070.73 |
|       |       |         | 125.32–252.99 | 256.00–1654.80| 393.01–6597.40| 108.81–1163.50 |
|       |       |         | 176.01 ± 39.04| 654.29 ± 409.43| 3742.4 ± 1860.3 | 457.15 ± 345.08|
|       |       |         |               |               |               | 1257.50 ± 1739.10 |
|       |       | BCF_B  | 0.0088–0.0255 | 0.0131–6.92   | 0.0338–4.875  | 0.0067–1.51   |
|       |       |         | 0.0137 ± 0.01 | 1.44 ± 2.09   | 0.2921 ± 0.15 | 0.4918 ± 0.55 |
|       |       |         |               |               |               | 0.5611 ± 1.21 |
|       |       | BCF_W  | 153.41–609.57 | 376.31–4001.80| 1318.67–16,874.94| 99.17–2943.52 |
|       |       |         | 364.94 ± 170.57| 1227.60 ± 987.62| 7230.87 ± 4190.34| 841.75 ± 832.42|
|       |       |         |               |               |               | 2416.30 ± 3554.50 |
### Table 5. Cont.

| Metal | River | Index | 2015       | 2016       | 2017       | 2018       |
|-------|-------|-------|------------|------------|------------|------------|
|       |       |       | Min–Max    | T ± SD     |           |            |
|       |       |       | Mn         | P          | B          | S          |
|       |       |       | 95.63–637.51 | 16.49–369.65 | 31.43–883.94 | 13.06–3955.12 |
|       |       |       | 245.13 ± 126.18 | 81.24 ± 69.17 | 148.99 ± 168.06 | 270.44 ± 711.32 |
|       |       |       | 186.45 ± 380.10 |           |            |            |
|       | NS    | BCF_p | 0.5156–2.76   | 0.0968–1.30  | 0.0901–4.96  | 0.0681–14.00 |
|       |       |       | 1.52 ± 0.66   | 0.4800 ± 0.31 | 1.03 ± 0.96  | 1.38 ± 2.50  |
|       |       |       | 1.08 ± 1.46   |           |            |            |
|       |       | BCF_w | 177.98–20,701.61 | 61.28–3252.45 | 59.91–7864.23 | 90.51–21,392.88 |
|       |       |       | 2870.61 ± 4392.15 | 608.91 ± 635.14 | 998.85 ± 1398.14 | 1853.58 ± 3840.08 |
|       |       |       | 1582.98 ± 3209.89 |           |            |            |
|       | P     | BCF_p | 110.03–189.34 | 128.09–196.99 | 35.44–1731.87 | 32.58–198.63 |
|       |       |       | 114.61 ± 20.37 | 166.63 ± 16.63 | 339.43 ± 380.89 | 114.55 ± 51.16 |
|       |       |       | 191.30 ± 211.55 |           |            |            |
|       |       | BCF_w | 0.6932–7.32    | 0.9175–4.30   | 0.1126–20.84  | 0.2788–35.58 |
|       |       |       | 2.84 ± 1.97    | 2.26 ± 1.03   | 2.82 ± 4.35   | 11.25 ± 11.54 |
|       |       |       | 4.79 ± 7.29    |           |            |            |
|       | Mn    | BCF_p | 389.10–1623.80 | 233.95–1419.03 | 43.64–6050.89 | 129.17–2254.06 |
|       |       |       | 913.29 ± 352.49 | 687.73 ± 342.06 | 937.72 ± 1170.59 | 867.17 ± 540.35 |
|       |       |       | 851.48 ± 696.75 |           |            |            |
|       | S     | BCF_p | 102.11–156.66  | 132.66–175.41 | 95.05–2135.80 | 12.03–195.91 |
|       |       |       | 134.22 ± 18.73 | 156.74 ± 14.17 | 505.61 ± 569.06 | 57.73 ± 60.57 |
|       |       |       | 213.58 ± 334.35 |           |            |            |
|       |       | BCF_w | 0.6215–1.28    | 0.6333–10.67  | 0.5574–13.90  | 0.1297–3.16 |
|       |       |       | 0.9692 ± 0.23  | 5.01 ± 4.09   | 3.59 ± 3.74   | 1.19 ± 0.84 |
|       |       |       | 2.69 ± 3.28    |           |            |            |
|       |       | BCF_w | 207.61–10,155.10 | 514.55–2106.89 | 361.19–7412.04 | 22.93–3092.28 |
|       |       |       | 1426.48 ± 2369.06 | 970.79 ± 437.83 | 1958.03 ± 2107.42 | 528.80 ± 847.89 |
|       |       |       | 1221.03 ± 1738.64 |           |            |            |

NS—Nysa Szalona River; B—Bystrzyca River; S—Strzegomka River; P—metal content in the plant; BCF_B—metals bioaccumulation factor—bottom sediment; BCF_W—metals bioaccumulation factor—water.

### 3.1.1. Copper

Throughout the study cycle, the range of copper content in reed canary grass was from 2.33 mgCu·kg⁻¹ to 396.55 mgCu·kg⁻¹, with a range for mean values of 7.92 mgCu·kg⁻¹–31.02 mgCu·kg⁻¹ (Table 5). The bioaccumulation factor with respect to bottom sediments ranged from BCF_B = 0.0090 to BCF_B = 13.13, and with respect to water it was higher, at a level of BCF_W = 30.47–82,142.29 (Table 5).

Statistically significant differences in copper content of reed canary grass were recorded between all rivers in each year with minor exceptions (Figure 2). These exceptions indicate that each year was different, and therefore inferences about environmental quality should be made during long-term studies. The long-term data allowed the identification of the Nysa Szalona River as having statistically higher levels of this metal.
3.1.1. Copper

Throughout the study, statistically significant differences were recorded between all rivers in each year with minor exceptions (Figure 2). These exceptions were indicated that both the Bystrzyca and Strzegomka have statistically the lowest cadmium content compared to the Nysa Szalona. However, in the reservoirs of the same region, whose catchment areas are strongly influenced by economic activity, the level of copper in plants was similar to that presented in this study [31–39]. However, in the reservoirs of the same region, whose catchment areas are strongly exposed to greater pollution or even contamination (copper mine), an increase in the level of this metal in aquatic plants can be observed [40].

Studies conducted in other parts of Poland and the world in moderately polluted areas show that although copper levels in plants were quite variable, they were similar to those recorded for the studied rivers [5,36,38,41–51].

3.1.2. Cadmium

Cadmium content in reed canary grass ranged from 0.0400 mgCd·kg−1 to 10.89 mgCd·kg−1 (Table 5). Mean values ranged from 0.8969 mgCd·kg−1 to 1.65 mgCd·kg−1. Cadmium bioaccumulation factor with respect to sediment (BCF_B = 0.0209–41.07) was lower than with respect to water (BCF_W = 5.35–18,155.50) (Table 5). In studies on the Strzegomka, Nysa Szalona and Bystrzyca Rivers conducted in previous years, the cadmium content in plants was similar to the results obtained in this study, with levels reaching a maximum of 8.80 mgCd·kg−1 [2,4,5,16,31,32,35,37–43,45–49,51,52]. This indicates a persistently stable level of cadmium in the environment and relatively unchanged water chemistry conditions. Higher concentrations were recorded in submerged plants or those growing in intensively polluted reservoirs such as post-mining pits, for example [33,34,36,53].

Statistically significant differences in cadmium levels in aquatic plants were found between all rivers only in the last year of the study (Figure 3). In contrast, no such differences were recorded between any rivers in 2016. The multiannual data obtained indicated that both the Bystrzyca and Strzegomka have statistically the lowest cadmium content compared to the Nysa Szalona.


![Cadmium Concentration](image)

**Figure 3.** Cd concentration in plants from rivers across 29 sites depending on river (graph to the left) and by year 2015–2018 in the table to the right. Statistically significant differences are marked in the graph with letters a, b and in the table these differences are shown by year between rivers—T—differences were present, F—no statistical difference (p-value ≤ 0.05).

### 3.1.3. Nickel

Nickel levels in all plant samples collected ranged from 0.1625 mgNi·kg⁻¹ to 31.67 mgNi·kg⁻¹ (Table 5). The mean values ranged between 5.12 mgNi·kg⁻¹ and 6.76 mgNi·kg⁻¹. The bioaccumulation of nickel determined with respect to bottom sediments was $BCF_B = 0.0041–1.57$, and a higher level was reached with respect to water, $BCF_W = 0.7329–13,014.50$ (Table 5).

The Bystrzyca River and the Slup Dam reservoir, into which the Nysa Szalona flows, were characterized in previous years by similar nickel levels to those presented in this study [2,4]. This indicates a fairly stable level of nickel in the studied environment, although in studies on the Nysa Szalona and Strzegomka carried out in earlier years the level of nickel was higher [34]. Higher levels of nickel were also found in submerged plants and those growing in artificial reservoirs, but also in mountainous and lowland areas subjected to anthropopression [36,40,50].

In general, in most of the studies presented, the range of nickel content in aquatic plants is similar to that recorded in this study and reaches a maximum threshold at 24.67 mgNi·kg⁻¹ [32,33,37–39,41,43,45,46,49,51,52,54].

Similar to cadmium, statistically significant differences in nickel levels between plants from different rivers were found in 2018 (Figure 4). In the remaining years, such differences were not observed, although in sum, without division into years, statistical differences were observed between the Bystrzyca, and the Nysa Szalona.

### 3.1.4. Lead

Lead levels in plants ranged from 1.63 mgPb·kg⁻¹ to 87.36 mgPb·kg⁻¹, with averages oscillating between 8.74 mgPb·kg⁻¹ and 22.26 mgPb·kg⁻¹ (Table 5). Bioaccumulation with respect to water was $BCF_W = 6.03–219,934.00$, and much less with respect to sediment $BCF_B = 0.0013–3.79$ (Table 5).

Similar values to the present results were noted for the same rivers in previous years, which as for nickel, copper and cadmium confirms relatively stable conditions present in the rivers for many years [2,4,16]. However, higher values were found in plants from mountainous regions, but also from highly industrialized and urbanized areas [34,38,40,48,53].

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**Table 5.** Statistical significance of differences between rivers in particular years (K-W)

| YEAR | '15 | '16 | '17 | '18 |
|------|-----|-----|-----|-----|
| Bystrzyca-Nysa Łużycka | T | F | T | T |
| Bystrzyca-Strzegomka | F | F | T | T |
| Nysa Łużycka-Strzegomka | T | F | F | T |

T-True  
F-False  
K-W-Kruskal-Wallis test (p-value ≤ 0.05)
Ni concentration in plants from rivers across 29 sites depending on river (graph to the left) and by year 2015–2018 in the table to the right. Statistically significant differences are marked in the graph with letters a, b and in the table these differences are shown by year between rivers—T—differences were present, F—no statistical difference (p-value ≤ 0.05).

Only in 2016, statistically significant differences in lead content in reed canary grass were found (Figure 5) between all studied rivers. In 2015 and 2018 such differences were found only between the Bystrzyca and the Nysa Szalona, and between the Nysa Szalona and the Strzegomka. The multiannual data collected allowed for the observation of the lowest amount of lead in the Strzegomka and the highest in the Nysa Szalona.

Figure 4. Ni concentration in plants from rivers across 29 sites depending on river (graph to the left) and by year 2015–2018 in the table to the right. Statistically significant differences are marked in the graph with letters a, b and in the table these differences are shown by year between rivers—T—differences were present, F—no statistical difference (p-value ≤ 0.05).

Figure 5. Pb concentration in plants from rivers across 29 sites depending on river (graph to the left) and by year 2015–2018 in the table to the right. Statistically significant differences are marked in the graph with letters a, b and in the table these differences are shown by year between rivers—T—differences were present, F—no statistical difference (p-value ≤ 0.05).

3.1.5. Zinc

The amount of zinc in reed canary grass ranged from 5.96 mgZn·kg⁻¹ to 206.54 mgZn·kg⁻¹, with a range for mean values of 44.54–4742.30 mgZn·kg⁻¹ (Table 5). Zinc accumulation in plants relative to sediment (BCF₈ = 0.0099–3.46) was lower than relative to water (BCF₈ = 13.84–70.158.80).

The level of zinc, similarly to the above-mentioned metals, in previous studies carried out in the area of the Slup reservoir into which the Nysa Szalona flows, was within a similar range as at present (8.00–80.10 mgZn·kg⁻¹) [2]. However, for the Nysa Szalona,
Strżegomka and Bystrzyca Rivers studied separately, the values found were higher (up to 700 mgZn kg\(^{-1}\)) [4,16]. Higher values were also found in the submontane regions of Lower Silesia and other rivers in southern Poland, as well as in the western border areas of Germany [32–34,38]. Higher values were also found in more industrialized regions [40,49]. Generally, in the majority of studies covering the European area and other parts of the world, the level of copper is similar to that recorded in this study [2,5,31,37,39,41–48,50–52,54,55].

Statistically significant differences in zinc content were recorded with one exception (year 2018, Nysa Szalona and Strżegomka) between all rivers (Figure 6). All the obtained data allowed this study to single out the Nysa Szalona River as the watercourse with the statistically lowest level of zinc.

![Zn concentration in plants from rivers across 29 sites depending on river](image)

Figure 6. Zn concentration in plants from rivers across 29 sites depending on river (graph to the left) and by year 2015–2018 in the table to the right. Statistically significant differences are marked in the graph with letters a, b and in the table these differences are shown by year between rivers—T—differences were present, F—no statistical difference (p-value ≤ 0.05).

3.1.6. Iron and Manganese

Iron levels in the aquatic plant samples ranged from 2.96 mgFe kg\(^{-1}\) to 6597.40 mgFe kg\(^{-1}\), with mean values of 461.31–1257.50 mgFe kg\(^{-1}\) (Table 5). Bioaccumulation of iron calculated relative to its level in water was BCF\(_W = 1.23–16,874.94\), and relative to bottom sediments it was lower, BCF\(_B = 0.0001–6.92\) (Table 5).

The manganese content in reed canary grass ranged from 12.03 mgMn kg\(^{-1}\) to 3955.12 mgMn kg\(^{-1}\) (Table 5). Mean values ranged from 186.45 mgMn kg\(^{-1}\) to 213.58 mgMn kg\(^{-1}\). Manganese bioaccumulation with respect to water was BCF\(_W = 22.93–21,392.88\), and with respect to bottom sediments it was BCF\(_B = 0.0681–35.58\) (Table 5).

The level of iron and manganese in plants studied in the Bystrzyca River remained within a similar range as in previous years [4]. Also in other rivers in this region of Poland the iron content in hydromacrophytes was similar [31–33,35,39,54]. Apart from that area, the recorded metal contents in aquatic plants were similar in other reservoirs [49,52,56].

However, significantly higher amounts were found in plants from the Nysa Szalona and Strżegomka Rivers studied several years earlier and in industrial areas, which indicates the anthropogenic origin of these metals [16,32,34,37,40,50].

Statistically significant differences in manganese content were noted between the Nysa Szalona and Strżegomka in each year of study (Figure 7). Statistically significant differences were recorded between the Bystrzyca and the Nysa Szalona. The exception was the year 2018, where these differences were not found, exactly the opposite statistical relationship was observed between the Bystrzyca and Strżegomka Rivers.

![Statistical significance of differences](image)

\[\text{STTSTATISTICAL SIGNIFICANCE OF DIFFERENCES BETWEEN RIVERS IN PARTICULAR YEARS (K-W)}\]

| YEAR | '15 | '16 | '17 | '18 |
|------|-----|-----|-----|-----|
| Bystrzyca-Nysa Łużycka | T | T | T | T |
| Bystrzyca-Strżegomka | T | T | T | T |
| Nysa Łużycka-Strżegomka | T | T | T | F |

T-True
F-False
K-W-Kruskal-Wallis test (p-value ≤ 0.05)

a, b—statistically significant differences, p-value ≤ 0.05
Mn concentration in plants from rivers across 29 sites depending on river (graph to the (left)) and by year 2015–2018 in the table to the (right). Statistically significant differences are marked in the graph with letters a, b and in the table these differences are shown by year between rivers—T—differences were present, F—no statistical difference (p-value ≤ 0.05).

In the case of iron, statistically significant differences in its content in the studied samples recorded between the three rivers do not allow to determine the regularity (Figure 8). The four-year study made it possible to show the Nysa Szalona as the river with the statistically lowest level of iron.

Fe concentration in plants from rivers across 29 sites depending on river (graph to the (left)) and by year 2015–2018 in the table to the (right). Statistically significant differences are marked in the graph with letters a, b and in the table these differences are shown by year between rivers—T—differences were present, F—no statistical difference (p-value ≤ 0.05).

The differences between the rivers may be noted using PCA plot. Nysa Szalona and Strzegomka were the most different in respect of the examined parameters, and Bystrzyca had parameters intermediate between the other rivers (Figure 9).
The differences between the rivers may be noted using PCA plot. Nysa Szalona and Strzegomka were the most different in respect of the examined parameters, and Bystrzyca had parameters intermediate between the other rivers (Figure 9).

Figure 9. PCA plot 2D showing clustering of metals concentration in plants from rivers across 29 sites and 4 years (2015–2018) grouping factor—river.

During the four-year study cycle, for all metals studied, the lowest values were recorded in the first (2015) and last (2018) year of the study, and the highest in 2017 (Table 5). Bioaccumulation of metals determined relative to bottom sediments was highest in 2017 and lowest in 2018, while bioaccumulation relative to water reached the highest values in 2018 and lowest in 2016. Using the PCA plot, differences between years can be seen, with the most varied results in 2015 and the least varied results in 2016 (Figure 10).

Figure 10. PCA plot 2D showing clustering of metals concentration in plants from rivers across 29 sites and 4 years (2015–2018) grouping factor—year.

3.2. Comparison of Metals Content—Source and Mouth of the River

Comparison of metal levels within the extreme sites on the main rivers shows that, for the most part, the estuaries of the rivers to the reservoirs in all study years had higher...
contents of the metals studied than the site below the springs (Table 6). This indicates enrichment with metal compounds of the main rivers by successively escaping tributaries. A similar relationship was found for the accumulation coefficient in relation to sediment. On the other hand, for the coefficient calculated in relation to metal concentration in water, sometimes higher values occurred at the site downstream of the springs.

Table 6. Metal content (mg kg\(^{-1}\)) of reed canary grass in three main rivers over a four-year study cycle.

| Metal | River | Index | 2015       | 2016       | 2017       | 2018       |
|-------|-------|-------|------------|------------|------------|------------|
|       |       |       | Min–Max    | \(\bar{x} \pm SD\) | Min–Max    | \(\bar{x} \pm SD\) | Min–Max    | \(\bar{x} \pm SD\) |
|       |       |       | 6.52–123.58 | 65.04 ± 58.51 | 5.48–9.46  | 7.47 ± 1.99 | 2.33–8.88  | 5.52 ± 3.12 |
| 1     | P     | 2     | 4.55–296.64 | 150.56 ± 145.99 | 6.54–10.98 | 8.57 ± 2.03 | 6.42–14.99 | 10.58 ± 4.16 |
| 1     | NS    |       | 0.0300–2.56 | 1.29 ± 1.26 | 0.0218–0.1918 | 0.1066 ± 0.09 | 0.0596–0.2670 | 0.4695–0.5126 |
| 2     | BCF\(_B\) | 0.0124–8.39 | 4.18 ± 4.17 | 0.0086–0.3014 | 0.1606 ± 0.04 | 0.4459–0.5360 | 0.1037–0.4351 |
| 1     | BCF\(_W\) | 1423.63–38,603.06 | 18,138.83 ± 11,318.37 | 56.26–149.66 | 103.11 ± 46.04 | 664.66–765.89 | 721.41 ± 35.21 |
| 2     | Cu    | 1263.28–57,011.29 | 28,629.02 ± 27,343.78 | 86.85–130.61 | 106.87 ± 19.74 | 1736.05–2918.31 | 2310.17 ± 544.12 |
| 1     | P     | 7.41–10.42 | 8.91 ± 1.50 | 6.36–6.96 | 6.20 ± 0.58 | 5.10–8.91 | 6.94 ± 1.83 |
| 2     | 12.44–12.53 | 12.48 ± 0.04 | 4.96–6.34 | 5.61 ± 0.65 | 13.25–19.93 | 16.39 ± 3.07 | 4.12–6.26 | 5.19 ± 1.07 |
| 1     | BCF\(_B\) | 0.0415–0.7355 | 0.3808 ± 0.34 | 0.0268–0.4555 | 0.2383 ± 0.21 | 0.2915–1.54 | 0.9089 ± 0.62 |
| 2     | 0.0264–2.77 | 1.36 ± 1.34 | 0.0107–1.14 | 0.5640 ± 0.55 | 0.3253–0.5954 | 0.4560 ± 0.13 | 0.0982–0.4772 |
| 1     | BCF\(_W\) | 4165.00–7412.30 | 4165.00–7412.30 | 1025.45–4024.50 | 1457.49–1579.14 | 1524.99 ± 42.73 | 63.21–72.62 |
| 2     | 2304.33–2722.46 | 2304.33–2722.46 | 2490.01 ± 1446.69 | 2490.01 ± 1446.69 | 1524.99 ± 42.73 | 68.86 ± 3.60 | 46.78–100.48 |
| 1     | 2516.33 ± 170.86 | 2516.33 ± 170.86 | 919.94–1441.41 | 919.94–1441.41 | 1949.13–4634.65 | 3239.59 ± 1252.31 | 71.98 ± 24.41 |
Table 6. Cont.

| Metal | River | Index | 2015            | 2016         | 2017         | 2018         |
|-------|-------|-------|-----------------|--------------|--------------|--------------|
|       |       |       | **Min–Max** τ ± SD |              |              |              |
| 1     | P     |       | 10.20–12.86     | 8.10–12.69   | 14.41–22.68  | 3.02–5.91    |
|       |       |       | 11.47 ± 1.04    | 10.52 ± 2.11 | 18.44 ± 3.84 | 4.39 ± 1.34  |
| 2     |       |       | 11.21 ± 5.51    |              |              |              |
|       |       |       | 13.01–13.99     | 11.33–29.89  | 9.34–15.55   | 3.85–7.88    |
|       |       |       | 13.52 ± 0.39    | 20.50 ± 9.10 | 12.45 ± 3.04 | 5.89 ± 1.97  |
|       |       |       | 13.09 ± 7.12    |              |              |              |
| Cu    | S     | BCF   | 0.6326–0.9718   | 0.6109–0.8718 | 1.09–1.30   | 0.2861–0.4684 |
|       |       |       | 0.7956 ± 0.15   | 0.7527 ± 0.12 | 1.19 ± 0.09 | 0.3718 ± 0.08 |
|       |       |       | 0.7775 ± 0.31   |              |              |              |
|       |       |       | 1.62–1.99       | 1.41–4.25    | 1.16–2.24    | 0.2281–1.11  |
|       |       |       | 1.81 ± 0.15     | 2.82 ± 1.39  | 1.70 ± 0.53  | 0.6708 ± 0.44 |
|       |       |       | 1.75 ± 1.09     |              |              |              |
|       |       | BCFW  | 3830.41–5589.87 | 3842.81–4519.43 | 6469.00–9448.13 | 30.47–98.15 |
|       |       |       | 4741.21 ± 769.29 | 4210.69 ± 239.62 | 7729.80 ± 1223.75 | 62.89 ± 32.16 |
|       |       |       | 4186.15 ± 2829.10 |              |              |              |
|       |       |       | 1717.95–2151.91 | 1934.78–4395.09 | 3155.33–3022.59 | 37.19–157.37 |
|       |       |       | 1938.34 ± 167.33 | 3126.59 ± 1179.91 | 2182.29 ± 798.35 | 97.34 ± 59.45 |
|       |       |       | 1836.14 ± 1311.52 |              |              |              |
| Cd    | NS    | BCF   | 0.5964–5.07     | 0.5632–0.8898 | 0.8212–0.9997 | 0.0984–1.02  |
|       |       |       | 2.83 ± 2.23     | 0.6264 ± 0.06 | 0.8662 ± 0.04 | 0.9991 ± 0.01 |
|       |       |       | 1.33 ± 1.42     |              |              |              |
|       |       |       | 1.21–8.24       | 0.6345–1.37  | 1.00–1.14    | 1.02–1.13    |
|       |       |       | 4.72 ± 3.51     | 0.9548 ± 0.32 | 1.08 ± 0.06  | 1.09 ± 0.04  |
|       |       |       | 1.96 ± 2.38     |              |              |              |
|       |       | BCFW  | 0.2263–5.10     | 0.2719–0.5904 | 0.4336–0.6485 | 0.8891–0.9650 |
|       |       |       | 2.66 ± 2.43     | 0.4299 ± 0.1573 | 0.5343 ± 0.1085 | 0.9284 ± 0.03 |
|       |       |       | 1.1379 ± 1.51   |              |              |              |
|       |       |       | 0.2503–8.74     | 0.2466–0.9958 | 0.8036–0.8387 | 1.06–1.13    |
|       |       |       | 4.49 ± 4.24     | 0.6224 ± 0.37 | 0.8197 ± 0.01 | 1.10 ± 0.02  |
|       |       |       | 1.7559 ± 2.65   |              |              |              |
|       |       | BCFW  | 993.02–2993.50  | 469.33–1371.00 | 1026.50–8997.00 | 32.19–1447.43 |
|       |       |       | 1662.95 ± 742.16 | 853.40 ± 375.53 | 5021.48 ± 3942.86 | 679.65 ± 650.08 |
|       |       |       | 2054.37 ± 2690.25 |              |              |              |
|       |       |       | 4048.33–7487.55 | 334.16–2462.20 | 1418.13–5010.00 | 25.71–27.56  |
|       |       |       | 5560.33 ± 1521.37 | 1300.12 ± 966.96 | 2720.15 ± 1345.65 | 26.66 ± 0.63  |
|       |       |       | 2401.82 ± 2344.83 |              |              |              |
|       |       |       | 0.7603–0.9544   | 0.7850–1.13  | 1.47–2.09    | 0.1001–2.34  |
|       |       |       | 0.8567 ± 0.09   | 0.9481 ± 0.16 | 1.77 ± 0.27  | 1.22 ± 0.12  |
|       |       | B     | 1.19 ± 0.68     |              |              |              |
|       |       |       | 1.00–1.12       | 1.01–1.02    | 1.19–1.50    | 0.0355–0.7485 |
|       |       |       | 1.06 ± 0.06     | 1.01 ± 0.01  | 1.35 ± 0.15  | 0.3916 ± 0.36 |
|       |       |       | 0.9511 ± 0.40   |              |              |              |
| Metal | River | Index | 2015          | 2016          | 2017          | 2018          |
|-------|-------|-------|---------------|---------------|---------------|---------------|
|       |       |       | Min–Max       |                |               |               |
|       |       |       | $\mu \pm SD$  |               |               |               |
|       |       |       | 0.3617–0.5671 | 0.3077–0.7835  | 1.4940–3.24   | 0.1657–2.20   |
| Cd    |       | 1     | 0.4635 ± 0.1015 | 0.5471 ± 0.24 | 2.34 ± 0.82   | 1.18 ± 1.01   |
|       |       | 2     | 0.2575–4.09    | 0.2454–4.01    | 0.6409–0.6796 | 0.0208–0.6454 |
|       |       |       | 2.14 ± 1.88    | 2.10 ± 1.86    | 0.6595 ± 0.02 | 0.3318 ± 0.31 |
|       |       | BCF_B | 1.13 ± 1.00    |               |               |               |
|       |       | BCF_W | 1.3088 ± 1.56  |               |               |               |
| B     |       | 1     | 1267.33–4772.00 | 1308.33–2202.00 | 2323.33–15,433.00 | 167.00–11,684.50 |
|       |       | 2     | 2571.62 ± 1256.67 | 1745.96 ± 375.38 | 8760.72 ± 6199.75 | 4636.95 ± 4633.66 |
|       |       |       | 4428.81 ± 4771.88 |               |               |               |
|       |       |       | 3237.04 ± 3946.18 |               |               |               |
| Cd    |       | 1     | 0.8623–0.9654  | 0.7521–0.8564  | 0.7521–1.71   | 0.2543–0.7455 |
|       |       | 2     | 0.9613–1.07    | 0.9641–0.9976  | 0.9945–1.23   | 0.4105–0.9645 |
|       |       |       | 1.01 ± 0.04    | 0.9807 ± 0.02  | 1.11 ± 0.11   | 0.6885 ± 0.27 |
|       |       |       | 0.8611 ± 0.37  |               |               |               |
| S     |       | 1     | 0.9978–1.30    | 0.8568–1.19    | 0.7617–2.70   | 0.2403–0.7725 |
|       |       | 2     | 1.1501         | 1.03 ± 0.17    | 1.74 ± 0.95   | 0.5054 ± 0.26 |
|       |       | BCF_B | 1.10 ± 0.67    |               |               |               |
|       |       | BCF_W | 1.61 ± 0.59    |               |               |               |
|       |       | 1     | 1070.44–8644.00 | 1423.50–7532.00 | 1504.20–17,076.00 | 5.36–21.79 |
|       |       | 2     | 4896.66 ± 3736.62 | 3899.49 ± 2688.94 | 9378.89 ± 7688.31 | 13.36 ± 7.97 |
|       |       |       | 4547.10 ± 5584.48 |               |               |               |
|       |       |       | 854.15 ± 617.60 |               |               |               |
| Ni    |       | 1     | 0.6325–6.46    | 5.00–5.57      | 3.42–7.09     | 5.33–8.99     |
|       |       | 2     | 3.55 ± 2.91    | 5.28 ± 0.28    | 5.24 ± 1.81   | 7.20 ± 1.54   |
|       |       | NS    | 5.32 ± 2.29    |               |               |               |
|       |       | 1     | 0.9621–14.58   | 6.11–6.56      | 4.76–9.99     | 5.41–9.37     |
|       |       | 2     | 7.75 ± 6.78    | 6.44 ± 0.16    | 7.30 ± 2.49   | 7.35 ± 1.89   |
|       |       |       | 7.21 ± 3.76    |               |               |               |
|       |       | BCF_B | 0.0993 ± 0.07  |               |               |               |
|       |       |       | 0.0287–0.0399  | 0.0134–0.2001  | 0.1604–0.1841 | 0.1178–0.2225 |
|       |       | 2     | 0.0343 ± 0.01  | 0.1050 ± 0.09  | 0.1726 ± 0.01 | 0.1684 ± 0.05 |
|       |       |       | 0.1201 ± 0.08  |               |               |               |
Table 6, Cont.

| Metal | River | Index | 2015           | 2016           | 2017           | 2018           |
|-------|-------|-------|----------------|----------------|----------------|----------------|
|       |       |       | Min–Max        | ± SD           |                |                |
|       |       |       | NS             | BCF<sub>W</sub> | BCF<sub>B</sub> | BCF<sub>W</sub> |
| 1     | 2     | 1     | 2102.00–4037.00 | 2227.72 ± 1557.25 | 0.2073–0.2713  | 0.2529 ± 0.31  |
|       |       | 2     | 5480.38–6587.00 | 5744.16 ± 411.29  | 0.0168–1.1192 | 0.0213–0.6688 |
|       |       |       | 4815–106.64    | 6.20 ± 0.78     | 6.12–13.44    | 0.6914–3.53    |
|       |       |       | 822.19–1531.15 | 9.74 ± 3.59     | 56.54–7256.98 | 42.15–3.12     |
|       |       |       | 76.76–943.87   | 3.07 ± 0.96     | 2106.94 ± 816.65 | 19.56–32.51 |
|       |       |       | 1325.68 ± 2244.52 | 4.25 ± 2.09  | 2896.60 ± 2107.68 | 0.3886 ± 0.45 |
|       |       |       | 43.35–1034.88  | 972.19–1272.81  | 594.19–1258.99 | 641.84 ± 625.55 |
|       |       | 1     | 5067.65 ± 1387.99 | 76.56 ± 28.20  | 2106.94 ± 816.65 | 0.3874–1.57  | 3.07 ± 0.96 |
|       |       | 2     | 5224.55 ± 4924.02 | 76.07 ± 29.51  | 1272.91 ± 324.99 | 9.29 ± 0.17  | 4.87 ± 1.44 |
|       |       |       | 1657.72 ± 3251.38 | 5.45–6.01     | 2896.60 ± 2107.68 | 3.41–6.45    | 9.12–9.56    |
|       |       |       | 1704.64 ± 2116.60 | 4.90 ± 0.48    | 2106.94 ± 816.65 | 8.07 ± 8.97  | 5.84 ± 0.23 |
|       |       |       | 3162.50–6458.70 | 4.30 ± 1.34    | 2106.94 ± 816.65 | 6.24 ± 0.09  | 3.45–6.01    |
|       |       |       | 5067.65 ± 1387.99 | 20.06 ± 11.26  | 2106.94 ± 816.65 | 0.2073–0.2713 | 0.3886 ± 0.45 |
|       |       |       | 3162.50–6458.70 | 2.95–5.65     | 20.06 ± 11.26  | 3.41–6.45    | 5.84 ± 0.23 |
|       |       |       | 4.15–106.64    | 4.90 ± 0.48    | 20.06 ± 11.26  | 3.41–6.45    | 5.84 ± 0.23 |
|       |       |       | 822.19–1531.15 | 8.66–31.67    | 20.06 ± 11.26  | 4.87 ± 1.44 |
|       |       |       | 822.19–1531.15 | 8.66–31.67    | 20.06 ± 11.26  | 4.87 ± 1.44 |
|       |       |       | 5067.65 ± 1387.99 | 20.06 ± 11.26  | 2106.94 ± 816.65 | 3.41–6.45    | 5.84 ± 0.23 |
|       |       |       | 5224.55 ± 4924.02 | 8.66–31.67    | 2106.94 ± 816.65 | 3.41–6.45    | 5.84 ± 0.23 |
|       |       |       | 1657.72 ± 3251.38 | 6.24 ± 0.09   | 2106.94 ± 816.65 | 3.41–6.45    | 5.84 ± 0.23 |
|       |       |       | 5067.65 ± 1387.99 | 6.24 ± 0.09   | 2106.94 ± 816.65 | 3.41–6.45    | 5.84 ± 0.23 |
|       |       |       | 5224.55 ± 4924.02 | 20.06 ± 11.26  | 2106.94 ± 816.65 | 3.41–6.45    | 5.84 ± 0.23 |
|       |       |       | 1657.72 ± 3251.38 | 20.06 ± 11.26  | 2106.94 ± 816.65 | 3.41–6.45    | 5.84 ± 0.23 |
### Table 6. Cont.

| Metal | River | Index | 2015     | 2016     | 2017     | 2018     |
|-------|-------|-------|----------|----------|----------|----------|
|       |       |       | Min–Max  |          |          |          |
|       |       |       | x ± SD   |          |          |          |
| Pb    | 1     | P     | 29.55–32.53 | 14.34–16.55 | 8.87–12.32 | 15.44–43.53 |
|       | 1     | BCF   | 31.05 ± 1.44 | 15.49 ± 1.05 | 10.58 ± 1.70 | 29.51 ± 13.78 |
|       | 2     | BCF   | 45.05–46.64 | 16.00–18.89 | 13.12–25.96 | 16.53–45.94 |
|       | 2     | BCF   | 45.74 ± 0.59 | 17.44 ± 1.30 | 19.37 ± 6.17 | 31.06 ± 14.30 |
|       |       | BCF   | 21.66 ± 11.25 |          |          |          |
|       |       | BCF   | 0.2361–1.01 | 0.6189 ± 0.38 | 0.1101–0.5334 | 0.3208 ± 0.21 |
|       |       | BCF   | 0.6189 ± 0.38 | 0.3208 ± 0.21 | 0.2153 ± 0.01 | 0.9617 ± 0.55 |
|       |       | BCF   | 0.2089–0.2209 | 0.2153 ± 0.01 | 0.2153 ± 0.01 | 0.9617 ± 0.55 |
|       |       | BCF   | 0.3999–1.53 | 0.9617 ± 0.55 |          |          |
|       |       | BCF   | 0.5292 ± 0.46 |          |          |          |
|       |       | BCF   | 0.2361–1.01 | 0.6189 ± 0.38 | 0.1101–0.5334 | 0.3208 ± 0.21 |
|       |       | BCF   | 0.1101–0.5334 | 0.3208 ± 0.21 | 0.2153 ± 0.01 | 0.9617 ± 0.55 |
|       |       | BCF   | 0.2089–0.2209 | 0.2153 ± 0.01 | 0.2153 ± 0.01 | 0.9617 ± 0.55 |
|       |       | BCF   | 0.3999–1.53 | 0.9617 ± 0.55 |          |          |
|       |       | BCF   | 0.5292 ± 0.46 |          |          |          |
|       |       | BCF   | 0.0013–0.0754 | 0.0174–0.4970 | 0.1918–0.4418 | 0.0821–0.1233 |
|       |       | BCF   | 0.0013–0.0754 | 0.0174–0.4970 | 0.1918–0.4418 | 0.0821–0.1233 |
|       |       | BCF   | 0.0382 ± 0.04 | 0.2516 ± 0.23 | 0.3158 ± 0.12 | 0.1017 ± 0.02 |
|       |       | BCF   | 0.0382 ± 0.04 | 0.2516 ± 0.23 | 0.3158 ± 0.12 | 0.1017 ± 0.02 |
|       |       | BCF   | 0.0174–0.4970 | 0.1918–0.4418 | 0.0818–0.1233 | 0.0818–0.1233 |
|       |       | BCF   | 0.0174–0.4970 | 0.1918–0.4418 | 0.0818–0.1233 | 0.0818–0.1233 |
|       |       | BCF   | 0.1768 ± 0.17 |          |          |          |
|       |       | BCF   | 0.0038–0.1155 | 0.0190–0.8283 | 0.0763–0.0861 | 0.0102–0.1388 |
|       |       | BCF   | 0.0590 ± 0.06 | 0.4163 ± 0.40 | 0.0815 ± 0.01 | 0.0744 ± 0.06 |
|       |       | BCF   | 0.0038–0.1155 | 0.0190–0.8283 | 0.0763–0.0861 | 0.0102–0.1388 |
|       |       | BCF   | 0.0590 ± 0.06 | 0.4163 ± 0.40 | 0.0815 ± 0.01 | 0.0744 ± 0.06 |
|       |       | BCF   | 0.1768 ± 0.17 |          |          |          |
|       |       | BCF   | 0.0038–0.1155 | 0.0190–0.8283 | 0.0763–0.0861 | 0.0102–0.1388 |
|       |       | BCF   | 0.0590 ± 0.06 | 0.4163 ± 0.40 | 0.0815 ± 0.01 | 0.0744 ± 0.06 |
|       |       | BCF   | 0.1768 ± 0.17 |          |          |          |
|       |       | BCF   | 3867.10–38,613.00 | 7812.33–24,963.20 | 10,594.56–219,934.00 | 2451.52–3869.75 |
|       |       | BCF   | 22,042.68 ± 11,725.19 | 15,522.88 ± 7471.81 | 96,694.78 ± 93,143.62 | 3146.22 ± 604.92 |
|       |       | BCF   | 34,351.64 ± 39,657.12 |          |          |          |
|       |       | BCF   | 10,925.36 ± 9064.33 |          |          |          |
Table 6. Cont.

| Metal | River | Index | 2015          | 2016          | 2017          | 2018          |
|-------|-------|-------|---------------|---------------|---------------|---------------|
|       |       |       | Min–Max       | ± SD          | Min–Max       | ± SD          |
|       |       |       | 1             | 2             | 1             | 2             |
|       |       |       | 6.45–9.08     | 7.52–8.91     | 7.16–15.98    | 3.91–7.52     |
|       |       |       | 7.78 ± 1.27   | 8.15 ± 0.52   | 11.58 ± 4.19  | 5.70 ± 1.76   |
|       |       |       |               |               |               | 8.30 ± 3.18   |
|       |       |       | 9.08–12.05    | 8.09–14.65    | 5.63–11.49    | 8.13–10.94    |
|       |       |       | 10.72 ± 1.34  | 11.39 ± 3.07  | 8.55 ± 2.89   | 9.44 ± 1.25   |
|       |       |       |               |               |               | 10.02 ± 2.55  |
|       |       |       | 0.1040–0.1436 | 0.1187–0.1339 | 0.1099–0.2563 | 0.0619–0.0997 |
|       |       |       |               |               |               | 0.1238 ± 0.02 |
|       |       |       |               |               |               | 0.1256 ± 0.01 |
|       |       |       |               |               |               | 0.1834 ± 0.07 |
|       |       |       |               |               |               | 0.0806 ± 0.02 |
|       |       |       | 0.1283 ± 0.05 |               |               |               |
|       |       |       | 0.1859–0.3607 | 0.1587–0.2591 | 0.1158–0.3516 | 0.0949–0.2194 |
|       |       |       | 0.2758 ± 0.08 | 0.2089 ± 0.05 | 0.2332 ± 0.12 | 0.1540 ± 0.07 |
|       |       |       | 1864.03–11,348.50 | 3008.56–12,733.14 | 2752.65–15,645.00 | 11.34–37.14 |
|       |       |       | 6214.70 ± 4282.28 | 7171.37 ± 4199.63 | 8646.56 ± 5814.11 | 24.12 ± 12.71 |
|       |       |       | 1892.38–4818.08 | 3842.36–6974.05 | 2157.64–2571.68 | 32.92–37.79 |
|       |       |       | 1987.77–2392.62 | 3842.36–6974.05 | 2157.64–2571.68 | 32.92–37.79 |
|       |       |       | 3311.41 ± 1383.98 | 5339.08 ± 1442.70 | 2335.32 ± 165.63 | 36.19 ± 1.57 |
|       |       |       | 207.77–2392.62 | 214.77–3631.36 | 420.79–4205.34 | 230.55–2398.60 |
|       |       |       | 1281.57 ± 1053.38 | 1898.25 ± 1681.41 | 3095.83 ± 1270.18 | 1300.29–1068.89 |
|       |       |       | 911.28–4399.61 | 291.36–4344.51 | 3614.31–4933.39 | 161.94–248.12 |
|       |       |       | 2647.15 ± 1729.75 | 2307.41 ± 2012.97 | 4282.17 ± 629.29 | 204.94 ± 42.02 |
|       |       |       | 49.23–50.42 | 70.00–125.94 | 119.54–132.93 | 26.14–70.24 |
|       |       |       | 49.89 ± 0.53 | 97.77 ± 27.62 | 126.00 ± 6.39 | 48.34 ± 21.86 |
|       |       |       | 80.50 ± 37.49 |               |               |               |
|       |       |       | 55.53–62.44 | 98.11–136.50 | 81.15–107.62 | 29.31–51.77 |
|       |       |       | 58.91 ± 3.38 | 117.43 ± 19.03 | 94.34 ± 12.89 | 40.49 ± 11.07 |
|       |       |       | 77.79 ± 32.62 |               |               |               |
| Metal | River | Index | 2015         | 2016         | 2017         | 2018         |
|-------|-------|-------|--------------|--------------|--------------|--------------|
|       |       |       | Min–Max  
\(\text{\(\tau\pm SD\)}\) |              |              |              |
| Zn    |       |       | 0.0181–0.9612 | 0.0578–2.51  | 1.1624–2.77  | 0.2324–1.52  |
|       |       |       | 0.4886 ± 0.47 | 1.28 ± 1.22  | 1.96 ± 0.79  | 0.8727 ± 0.64|
|       |       | BCF_B | 0.0274–1.42   | 0.0443–3.41  | 0.3857–0.4457| 0.1492–0.7739|
|       |       |       | 0.7147 ± 0.69 | 1.72 ± 1.67  | 0.4152 ± 0.03| 0.4602 ± 0.31|
|       |       | BCF_W | 1946.53–4337.12 | 2602.36–10,075.50 | 5559.95–6989.95 | 153.49–1513.40 |
|       |       |       | 3123.72 ± 1169.94 | 6307.95 ± 3696.84 | 6270.12 ± 697.66 | 422.49 ± 489.29 |
|       |       |       | 0.8268 ± 1.06  |              |              |              |
|       |       | P     | 45.65–56.86   | 70.01–96.87  | 88.27–108.90 | 10.00–38.36  |
|       |       |       | 51.23 ± 5.46  | 83.28 ± 13.22| 98.59 ± 10.00| 24.18 ± 14.00|
|       |       | S     | 0.7320–0.9009 | 1.05–1.54    | 1.42–1.67    | 0.1318–0.6073|
|       |       |       | 0.8156 ± 0.08 | 1.29 ± 0.24  | 1.55 ± 0.12  | 0.3696 ± 0.24|
|       |       | BCF_B | 1.249–1.78    | 1.17–2.01    | 2.14–2.34    | 0.1988–1.05  |
|       |       |       | 1.50 ± 0.27   | 1.59 ± 0.41  | 2.24 ± 0.07  | 0.6265 ± 0.42|
|       |       | BCF_W | 656.87–4704.34 | 6108.96–70,157.80 | 4927.71–8198.44 | 21.00–55.57  |
|       |       |       | 2624.88 ± 1947.41 | 5083.80 ± 29,164.60 | 6626.96 ± 1552.14 | 38.18 ± 16.81 |
|       |       |       | 11,093.50 ± 20,286.70 |              |              |              |
|       |       | P     | 5.63–256.55   | 120.00–263.56 | 101.60–15,003.89 | 326.74–350.99|
|       |       |       | 131.04 ± 125.40 | 191.98 ± 71.53 | 802.59 ± 700.83 | 338.70 ± 11.91|
|       |       | S     | 6.33–469.53   | 113.53–270.45 | 16.26–256.57 | 86.09–369.68 |
|       |       |       | 237.83 ± 231.49 | 192.01 ± 78.31 | 136.32 ± 120.04 | 227.86 ± 141.58|
|       |       | BCF_B | 0.0002–0.0177 | 0.0072–0.0094 | 0.0026–0.0994 | 0.0209–0.0239|
|       |       |       | 0.0089 ± 0.0087 | 0.0083 ± 0.0011 | 0.0510 ± 0.05 | 0.0224 ± 0.01|
|       |       | BCF_W | 0.0003–0.0266 | 0.0065–0.1510 | 0.0010–0.0989 | 0.0047–0.0212|
|       |       |       | 0.0134 ± 0.01  | 0.0108 ± 0.0043 | 0.0401 ± 0.04 | 0.0129 ± 0.01|
|       |       |       | 0.0193 ± 0.03  |              |              |              |
Table 6. Cont.

| Metal | River | Index | 2015               | 2016               | 2017               | 2018               |
|-------|-------|-------|--------------------|--------------------|--------------------|--------------------|
|       |       |       | Min–Max            | Min–Max            | Min–Max            | Min–Max            |
|       |       |       | \( \mu \pm SD \)    | \( \mu \pm SD \)    | \( \mu \pm SD \)    | \( \mu \pm SD \)    |
|       |       |       | 21.11–251.25       | 119.70–1048.74     | 126.99–1501.24     | 207.91–517.49      |
|       |       |       | \( 136.11 \pm 114.86 \) | \( 576.86 \pm 456.69 \) | \( 813.36 \pm 686.22 \) | \( 361.53 \pm 153.39 \) |
| NS    | BCFW  | 1     | \( 471.96 \pm 492.12 \) | \( 6.57–958.03 \)  | \( 200.90–280.79 \)  | \( 24.94–2486.50 \)  | \( 165.91–758.57 \) |
|       |       | 2     | \( 480.73 \pm 474.15 \) | \( 240.71 \pm 39.33 \) | \( 973.17 \pm 1068.21 \) | \( 459.77 \pm 292.11 \) |
|       |       |       | \( 538.59 \pm 659.53 \) | \( \) | \( \) | \( \) |
|       | BCFB  | 1     | \( 365.41–452.99 \) | \( 521.01–692.91 \) | \( 686.25–5081.90 \) | \( 87.11–652.64 \) |
|       |       |       | \( 408.99 \pm 43.35 \) | \( 606.71 \pm 85.63 \) | \( 2833.98 \pm 2197.45 \) | \( 369.85 \pm 282.41 \) |
|       |       |       | \( 1067.38 \pm 1528.89 \) | \( \) | \( \) | \( \) |
|       | P     | 1     | \( 406.09–632.98 \) | \( 201.34–769.99 \) | \( 3251.47–4206.89 \) | \( 413.15–452.19 \) |
|       |       |       | \( 519.42 \pm 113.10 \) | \( 485.52 \pm 284.11 \) | \( 3729.08 \pm 477.51 \) | \( 432.74 \pm 19.41 \) |
|       |       |       | \( 1291.69 \pm 1435.87 \) | \( \) | \( \) | \( \) |
|       | BCFB  | 2     | \( 0.0397 \pm 0.01 \) | \( 0.0474 \pm 0.01 \) | \( 0.2426 \pm 0.20 \) | \( 0.6257 \pm 0.62 \) |
|       |       |       | \( 0.2388 \pm 0.40 \) | \( \) | \( \) | \( \) |
|       | Fe    | BCFW  | \( 226.50–2788.79 \) | \( 348.73–517.88 \) | \( 472.34–4535.96 \) | \( 32.82–322.23 \) |
|       |       |       | \( 671.64 \pm 933.91 \) | \( 433.67 \pm 84.26 \) | \( 2447.62 \pm 1975.95 \) | \( 177.47 \pm 144.37 \) |
|       |       |       | \( 932.57 \pm 1413.08 \) | \( \) | \( \) | \( \) |
|       |       | 1     | \( 411.40–511.87 \) | \( 233.25–573.68 \) | \( 3607.13–4288.67 \) | \( 437.79–1496.85 \) |
|       |       |       | \( 462.39 \pm 49.30 \) | \( 402.98 \pm 169.53 \) | \( 3941.56 \pm 334.12 \) | \( 964.68 \pm 526.57 \) |
|       |       |       | \( 1442.56 \pm 1494.56 \) | \( \) | \( \) | \( \) |
|       |       | 2     | \( 125.32–222.88 \) | \( 496.05–613.34 \) | \( 4907.10–4963.90 \) | \( 144.23–1163.50 \) |
|       |       |       | \( 174.04 \pm 48.46 \) | \( 554.80 \pm 58.43 \) | \( 4935.40 \pm 27.99 \) | \( 653.95 \pm 509.40 \) |
|       |       |       | \( 1579.50 \pm 1962.80 \) | \( \) | \( \) | \( \) |
|       | P     | 1     | \( 221.03–252.99 \) | \( 512.77–1654.80 \) | \( 2031.20–5006.40 \) | \( 222.15–854.89 \) |
|       |       |       | \( 237.13 \pm 15.66 \) | \( 1083.60 \pm 570.77 \) | \( 3518.80 \pm 1487.40 \) | \( 538.50 \pm 316.02 \) |
|       |       |       | \( 1344.50 \pm 1525.60 \) | \( \) | \( \) | \( \) |
|       |       | 1     | \( 0.0088–0.0165 \) | \( 0.0338–2.02 \)  | \( 0.3392–0.3969 \) | \( 0.0869–0.4774 \) |
|       |       |       | \( 0.0126 \pm 0.01 \) | \( 1.03 \pm 0.9934 \) | \( 0.3680 \pm 0.03 \) | \( 0.2815 \pm 0.1946 \) |
|       |       |       | \( 0.4223 \pm 0.63 \) | \( \) | \( \) | \( \) |
|       | S     | BCFB  | \( 0.0176–0.0255 \) | \( 0.0409–6.92 \)  | \( 0.2063–0.4613 \) | \( 0.0727–0.9682 \) |
|       |       |       | \( 0.0215 \pm 0.01 \) | \( 3.48 \pm 3.44 \) | \( 0.3338 \pm 0.13 \) | \( 0.5196 \pm 0.45 \) |
|       |       |       | \( 1.09 \pm 2.22 \) | \( \) | \( \) | \( \) |
|       |       | 2     | \( 490.32–609.57 \) | \( 1097.77–1677.41 \) | \( 11633.22–16874.94 \) | \( 404.46–2943.52 \) |
|       |       |       | \( 549.77 \pm 58.65 \) | \( 1377.47 \pm 278.28 \) | \( 14123.69 \pm 2481.96 \) | \( 1669.22 \pm 1262.44 \) |
|       |       |       | \( 4430.04 \pm 5783.56 \) | \( \) | \( \) | \( \) |
|       |       |       | \( 390.58–557.27 \) | \( 780.10–4001.80 \) | \( 4726.72–9561.52 \) | \( 601.37–1884.72 \) |
|       |       | 2     | \( 473.06 \pm 81.18 \) | \( 2387.49 \pm 1605.16 \) | \( 7069.07 \pm 2319.89 \) | \( 1246.37 \pm 633.58 \) |
|       |       |       | \( 2793.99 \pm 2940.65 \) | \( \) | \( \) | \( \) |
| Metal | River | Index | 2015 Min–Max | 2016 Min–Max | 2017 Min–Max | 2018 Min–Max |
|-------|-------|-------|--------------|--------------|--------------|--------------|
|       |       |       | 1            | 2            | 1            | 2            |
|       |       |       | t ± SD       | t ± SD       | t ± SD       | t ± SD       |
|       |       |       | P            | BCF          | P            | BCF          |
|       |       |       | 95.63–365.96 | 40.05–153.63 | 79.04–254.13 | 156.43–290.79 |
|       |       |       | 230.63 ± 134.88 | 97.03 ± 56.54 | 166.72 ± 87.37 | 223.47 ± 66.84 |
|       |       |       | 252.01–637.51 | 36.45–155.91 | 45.67–883.94 | 123.52–296.45 |
|       |       |       | 444.81 ± 192.49 | 96.10 ± 59.59 | 464.63 ± 418.87 | 210.00 ± 86.31 |
|       |       |       | 303.89 ± 283.67 |  |  |  |
|       |       |       | 0.5156–1.83 | 0.2315–0.5782 | 0.0901–1.35 | 1.01–1.63 |
|       |       |       | 1.17 ± 0.66 | 0.4056 ± 0.1722 | 0.7190 ± 0.63 | 1.32 ± 0.31 |
|       |       |       | 0.9041 ± 0.61 |  |  |  |
|       |       |       | 1.40–1.96 | 0.1922–0.5364 | 0.1423–4.96 | 0.4939–1.64 |
|       |       |       | 1.68 ± 0.28 | 0.3643 ± 0.17 | 2.55 ± 2.41 | 1.07 ± 0.57 |
|       |       |       | 1.42 ± 1.48 |  |  |  |
|       |       |       | 567.56–2966.96 | 244.83–1058.07 | 633.85–1587.54 | 1354.12–1890.82 |
|       |       |       | 1741.59 ± 1164.02 | 645.09 ± 398.86 | 1094.89 ± 459.81 | 1611.82 ± 243.05 |
|       |       |       | 1273.35 ± 797.64 |  |  |  |
|       |       |       | 2184.50–4381.52 | 233.86–1241.07 | 269.77–7864.23 | 831.26–2643.55 |
|       |       |       | 3127.81 ± 949.03 | 730.59 ± 494.20 | 3935.16 ± 3660.68 | 1739.42 ± 893.07 |
|       |       |       | 2383.24 ± 2315.79 |  |  |  |
|       |       |       | 125.33–165.79 | 165.44–193.95 | 306.99–1731.87 | 64.00–193.95 |
|       |       |       | 145.54 ± 20.17 | 179.58 ± 13.96 | 1019.63 ± 712.04 | 128.92 ± 64.59 |
|       |       |       | 368.42 ± 519.26 |  |  |  |
|       |       |       | 163.09–189.34 | 163.00–166.94 | 239.15–955.98 | 32.57–148.96 |
|       |       |       | 176.22 ± 12.93 | 154.12 ± 1.76 | 597.57 ± 358.08 | 90.58 ± 59.93 |
|       |       |       | 257.37 ± 269.44 |  |  |  |
|       |       |       | 0.9227–4.57 | 1.22–4.30 | 1.53–20.84 | 0.29–21.47 |
|       |       |       | 2.74 ± 1.81 | 2.75 ± 1.52 | 11.15 ± 9.62 | 10.88 ± 10.58 |
|       |       |       | 6.87 ± 8.34 |  |  |  |
|       |       |       | 1.33–3.37 | 1.29–2.6377 | 1.92–2.1983 | 0.31–29.79 |
|       |       |       | 2.34 ± 1.01 | 1.96 ± 0.67 | 2.05 ± 0.14 | 13.65 ± 13.42 |
|       |       |       | 5.00 ± 8.39 |  |  |  |
|       |       |       | 389.10–1090.69 | 237.03–531.98 | 540.32–4111.76 | 129.17–1310.00 |
|       |       |       | 735.73 ± 345.71 | 453.23 ± 103.12 | 2310.95 ± 1766.90 | 610.18 ± 403.06 |
|       |       |       | 1027.52 ± 1188.58 |  |  |  |
|       |       |       | 860.29–1307.91 | 238.71–875.25 | 424.63–3706.82 | 194.73–1613.91 |
|       |       |       | 1081.87 ± 220.69 | 554.02 ± 314.64 | 1699.80 ± 1325.57 | 873.63 ± 677.29 |
|       |       |       | 1052.33 ± 875.20 |  |  |  |
|       |       |       | 1125.52–145.99 | 152.56–156.96 | 212.45–2155.80 | 12.03–195.91 |
|       |       |       | 129.16 ± 16.49 | 154.64 ± 2.03 | 1184.00 ± 971.47 | 103.98 ± 91.67 |
|       |       |       | 392.95 ± 668.61 |  |  |  |
|       |       |       | 121.06–155.90 | 165.06–169.88 | 310.05–543.88 | 25.33–153.57 |
|       |       |       | 138.52 ± 17.14 | 167.62 ± 2.11 | 427.06 ± 116.65 | 89.49 ± 63.85 |
|       |       |       | 205.67 ± 147.01 |  |  |  |
Table 6. Cont.

| Metal | River | Index | 2015          | 2016          | 2017          | 2018          |
|-------|-------|-------|---------------|---------------|---------------|---------------|
|       |       |       | Min–Max       | x ± SD        | Min–Max       | x ± SD        |
| Mn    |       | 1     | 0.7196–1.13   | 1.12–8.60     | 1.65–13.91    | 7.75–130.36   |
|       |       |       | 0.92 ± 0.20   | 4.86 ± 3.73   | 7.77 ± 6.12   | 68.98 ± 61.22 |
|       |       | 2     | 1.12–1.28     | 1.22–9.39     | 2.34–5.20     | 1.16–3.16     |
|       |       |       | 1.20 ± 0.08   | 5.30 ± 4.08   | 3.77 ± 1.42   | 2.12 ± 0.95   |
|       | S     |       | 3.77 ± 4.52   |               |               |               |
|       |       | 1     | 420.79–1592.16| 514.55–2106.88| 462.29–7412.04| 38.54–3092.28 |
| Mn    |       |       | 977.06 ± 553.53| 1279.85 ± 764.66| 3882.99 ± 3417.81| 1495.17 ± 1457.92|
|       |       | 2     | 1908.77 ± 2237.76|               |               |               |
|       |       |       | 515.33–1177.46| 833.96–866.77 | 1666.21–4476.28| 167.87–883.92 |
|       |       |       | 846.75 ± 327.44| 852.94 ± 12.24| 3032.40 ± 1352.35| 518.86 ± 349.48|
| S     |       |       | 1312.74 ± 1232.65|               |               |               |

NS—Nysa Szalona River; B—Bystrzyca River; S—Strzegomka River; 1—river below its source; 2—river mouth to the reservoir; P—metal content in the plant; BCF<sub>B</sub>—metals bioaccumulation factor—bottom sediment; BCF<sub>W</sub>—metals bioaccumulation factor—water.

Metal contents also varied with the seasons. In the Strzegomka River at both extreme sites, higher amounts of Cu, Ni, Cd, Pb and Mn were recorded in autumn, and Zn and Fe in spring (Table 7). The Bystrzyca River had higher values for all metals at the reservoir outlet in spring (Table 8). Below the springs, there was a differentiation: in spring, higher levels of cadmium, lead and zinc were recorded, whereas the remaining metals predominated in autumn. On the other hand, in the Nysa Szalona River at both sites, copper and cadmium were more abundant in the spring, and higher amounts for the other metals were recorded in the autumn (Table 9).

Table 7. Metals (mg kg<sup>−1</sup>) and metal bioaccumulation factors relative to water (BCF<sub>W</sub>) and bottom sediment (BCF<sub>B</sub>) in reed canary grass in successive tributaries of the Strzegomka River in spring and autumn (mean values).

| Site               | Season | Index | Cu  | Cd  | Ni  | Pb  | Zn  | Fe  | Mn  |
|--------------------|--------|-------|-----|-----|-----|-----|-----|-----|-----|
|                    |        |       |     |     |     |     |     |     |     |
| Polska Woda        | s      | P     | 10.30| 0.71| 5.06| 6.38| 72.26| 1687.20| 177.63|
|                    |        | BCF<sub>B</sub> | 0.7833| 0.7232| 0.2326| 0.10| 1.13| 0.1172| 1.35|
|                    |        | BCF<sub>W</sub> | 4037.81| 1094.08| 328.29| 1970.11| 2983.41| 4041.98| 1747.57|
|                    | s      | P     | 12.11| 1.02| 11.08| 10.23| 56.38| 1471.90| 608.27|
|                    |        | BCF<sub>B</sub> | 0.7717| 1.49| 0.5447| 0.1561| 0.8763| 0.7275| 6.19|
|                    |        | BCF<sub>W</sub> | 4334.50| 8000.12| 2323.08| 9058.27| 19,203.50| 4818.09| 2069.96|
| Polska Woda        | a      | P     | 10.82| 0.5710| 4.74| 7.67| 89.80| 549.32| 133.34|
|                    |        | BCF<sub>B</sub> | 0.8274| 0.7061| 0.2492| 0.0883| 1.04| 0.0339| 0.9330|
|                    |        | BCF<sub>W</sub> | 1711.67| 821.66| 374.40| 2373.17| 3530.49| 1643.79| 1003.96|
| Polska Woda        | s      | P     | 9.86| 0.7800| 5.11| 9.39| 56.49| 246.34| 107.69|
|                    |        | BCF<sub>B</sub> | 0.9206| 1.17| 0.2329| 0.1407| 343.07| 0.2610| 2.82|
|                    |        | BCF<sub>W</sub> | 1464.08| 1056.72| 745.95| 5222.26| 68.52| 678.77| 424.56|
Table 7. Cont.

| Site                     | Season | Index | Cu  | Cd   | Ni   | Pb   | Zn   | Fe    | Mn    |
|--------------------------|--------|-------|-----|------|------|------|------|-------|-------|
| Sikorka                  | s      | P     | 11.29 | 0.9400 | 4.62 | 7.12 | 67.79 | 1867.00 | 136.65 |
|                          |        |       |      | 1.27 | 1.20 | 0.2134 | 0.0738 | 0.7040 | 0.1225 | 0.6572 |
|                          |        | BCF_B | 1372.16 | 1381.80 | 355.95 | 1694.61 | 2287.88 | 1871.09 | 2446.56 |
|                          |        | BCF_W | 14.66 | 1.08 | 9.45 | 9.58 | 79.00 | 1163.40 | 219.54 |
|                          | a      | P     | 1.36 | 1.51 | 0.3947 | 0.1325 | 1.16 | 0.8479 | 3.26 |
|                          |        |       |      | 1581.53 | 1211.68 | 1822.96 | 8294.48 | 4369.11 | 2042.19 | 375.59 |
| Czyżynka                 | s      | P     | 9.48 | 1.07 | 5.82 | 7.41 | 63.46 | 1104.60 | 219.54 |
|                          |        |       |      | 0.9433 | 1.26 | 0.2859 | 0.1195 | 1.01 | 0.0707 | 0.8605 |
|                          |        | BCF_B | 1776.63 | 1319.54 | 556.17 | 1905.26 | 2270.06 | 1168.16 | 899.52 |
|                          | a      | P     | 14.18 | 0.8900 | 7.67 | 9.54 | 47.89 | 1795.70 | 202.75 |
|                          |        |       |      | 1819.77 | 1201.47 | 1436.06 | 5560.19 | 2310.72 | 617.05 |
|                          | s      | P     | 12.12 | 0.8611 | 6.26 | 8.50 | 81.95 | 1648.80 | 196.23 |
|                          |        |       |      | 1.68 | 1.33 | 0.3279 | 0.1707 | 1.65 | 0.1482 | 1.50 |
|                          |        | BCF_B | 1795.60 | 1165.92 | 347.92 | 2090.33 | 3218.96 | 3110.24 | 1141.93 |
|                          | a      | P     | 14.06 | 1.04 | 6.21 | 11.54 | 53.45 | 1040.30 | 215.11 |
|                          |        |       |      | 1.82 | 1.28 | 0.2989 | 0.2652 | 1.33 | 2.03 | 4.69 |
|                          | s      | P     | 12.12 | 0.8611 | 6.26 | 8.50 | 81.95 | 1648.80 | 196.23 |
|                          |        |       |      | 1.68 | 1.33 | 0.3279 | 0.1707 | 1.65 | 0.1482 | 1.50 |
|                          |        | BCF_B | 1795.60 | 1165.92 | 347.92 | 2090.33 | 3218.96 | 3110.24 | 1141.93 |
|                          | a      | P     | 14.06 | 1.04 | 6.21 | 11.54 | 53.45 | 1040.30 | 215.11 |
| Strzegomka              | mouth to the reservoir | s      | P     | 6.22 | 1.34 | 4.79 | 14.85 | 83.41 | 415.17 | 165.77 |
|                          |        |       |      | 0.4935 | 1.27 | 0.2322 | 0.2088 | 1.21 | 0.0321 | 0.9941 |
|                          |        | BCF_W | 3174.44 | 6717.68 | 2352.17 | 57406.38 | 5468.21 | 535.64 | 458.81 |
|                          | a      | P     | 7.89 | 1.05 | 5.77 | 12.41 | 77.60 | 1719.59 | 571.06 |
|                          |        |       |      | 0.6319 | 0.9984 | 0.2737 | 0.1448 | 1.08 | 0.4456 | 12.76 |
|                          | s      | P     | 8.27 | 1.02 | 4.85 | 16.39 | 94.12 | 545.72 | 169.20 |
|                          |        |       |      | 0.6213 | 1.80 | 0.4570 | 0.1977 | 1.15 | 0.0476 | 1.14 |
|                          | a      | P     | 7.63 | 0.7564 | 3.30 | 12.18 | 70.20 | 687.68 | 268.28 |
| Strzegomka              | mouth to the reservoir | a      | P     | 7.63 | 0.7564 | 3.30 | 12.18 | 70.20 | 687.68 | 268.28 |
|                          |        |       |      | 0.5351 | 1.45 | 0.3210 | 0.1512 | 0.8652 | 0.4259 | 7.66 |
|                          | s      | P     | 1576.38 | 1742.05 | 1364.94 | 7337.48 | 8874.15 | 533.96 | 992.46 |

s—spring, a—autumn, P—metal content in the plant; BCF_B—metals bioaccumulation factor—bottom sediment; 
BCF_W—metals bioaccumulation factor—water

Table 8. Metals (mg kg$^{-1}$) and metal bioaccumulation factors relative to water (BCF_W) and bottom sediment (BCF_B) in reed canary grass in successive tributaries of the Bystrzyca River in spring and autumn (mean values).

| Site                     | Season | Index | Cu  | Cd   | Ni   | Pb   | Zn   | Fe    | Mn    |
|--------------------------|--------|-------|-----|------|------|------|------|-------|-------|
| Bystrzyca below springs  | s      | P     | 6.22 | 1.34 | 4.79 | 14.85 | 83.41 | 415.17 | 165.77 |
|                          |        |       |      | 0.4935 | 1.27 | 0.2322 | 0.2088 | 1.21 | 0.0321 | 0.9941 |
|                          |        | BCF_W | 3174.44 | 6717.68 | 2352.17 | 57406.38 | 5468.21 | 535.64 | 458.81 |
|                          | a      | P     | 7.89 | 1.05 | 5.77 | 12.41 | 77.60 | 1719.59 | 571.06 |
|                          |        |       |      | 0.6319 | 0.9984 | 0.2737 | 0.1448 | 1.08 | 0.4456 | 12.76 |
| Złoty Potok             | s      | P     | 8.27 | 1.02 | 4.85 | 16.39 | 94.12 | 545.72 | 169.20 |
|                          |        |       |      | 0.6213 | 1.80 | 0.4570 | 0.1977 | 1.15 | 0.0476 | 1.14 |
|                          | a      | P     | 7.63 | 0.7564 | 3.30 | 12.18 | 70.20 | 687.68 | 268.28 |
|                          | s      | P     | 2131.25 | 5943.15 | 2201.22 | 12142.10 | 4140.68 | 518.16 | 503.09 |
|                          | a      | P     | 7.63 | 0.7564 | 3.30 | 12.18 | 70.20 | 687.68 | 268.28 |
|                          | s      | P     | 1576.38 | 1742.05 | 1364.94 | 7337.48 | 8874.15 | 533.96 | 992.46 |
| Site          | Season | Index | Cu   | Cd   | Ni   | Pb   | Zn   | Fe   | Mn   |
|--------------|--------|-------|------|------|------|------|------|------|------|
| Klobia       | s      | P     | 8.46 | 0.9388 | 5.30 | 17.05 | 89.21 | 1083.46 | 150.64 |
|              |        | BCF<sub>B</sub> | 0.3990 | 1.06 | 0.2667 | 0.2048 | 0.9493 | 0.1175 | 0.9691 |
|              |        | BCF<sub>W</sub> | 3596.49 | 6225.83 | 2482.41 | 12,210.10 | 3805.27 | 951.33 | 768.89 |
|              | a      | P     | 7.16 | 0.7282 | 3.72 | 10.24 | 67.12 | 653.10 | 170.42 |
|              |        | BCF<sub>B</sub> | 0.7448 | 0.9555 | 0.1969 | 0.11 | 0.8091 | 0.7957 | 8.92 |
|              |        | BCF<sub>W</sub> | 1603.51 | 1966.61 | 1899.68 | 6915.97 | 3220.96 | 594.54 | 549.43 |
| Otłuczyna    | s      | P     | 8.45 | 0.8967 | 4.32 | 17.19 | 100.09 | 594.76 | 138.79 |
|              |        | BCF<sub>B</sub> | 0.4574 | 1.63 | 0.3814 | 0.2923 | 1.68 | 0.0579 | 0.8988 |
|              |        | BCF<sub>W</sub> | 4623.78 | 4974.69 | 2067.74 | 14,035.75 | 4705.91 | 525.13 | 799.02 |
|              | a      | P     | 5.01 | 0.7996 | 4.04 | 14.61 | 50.04 | 596.33 | 170.42 |
|              |        | BCF<sub>B</sub> | 0.2959 | 1.40 | 0.3957 | 0.2483 | 0.8194 | 0.7957 | 8.92 |
|              |        | BCF<sub>W</sub> | 1013.38 | 2395.95 | 2220.69 | 8939.17 | 2274.85 | 882.01 | 521.66 |
| Potok Marcowy Duży | s      | P     | 6.22 | 0.6389 | 7.46 | 12.69 | 70.77 | 309.96 | 104.91 |
|              |        | BCF<sub>B</sub> | 0.6158 | 0.9667 | 0.5000 | 0.2992 | 1.56 | 0.0328 | 0.8144 |
|              |        | BCF<sub>W</sub> | 2487.10 | 2746.72 | 3399.60 | 9019.40 | 3425.44 | 368.81 | 839.35 |
|              | a      | P     | 4.83 | 0.8333 | 4.96 | 8.98 | 43.05 | 412.27 | 149.73 |
|              |        | BCF<sub>B</sub> | 0.2013 | 0.8122 | 0.1518 | 0.0984 | 0.6191 | 0.3439 | 6.67 |
|              |        | BCF<sub>W</sub> | 1451.23 | 4345.64 | 2644.82 | 5215.77 | 2467.25 | 1475.80 | 1051.07 |
| Złota Woda   | s      | P     | 4.70 | 0.5986 | 3.76 | 12.81 | 56.13 | 207.40 | 115.94 |
|              |        | BCF<sub>B</sub> | 0.3904 | 1.45 | 0.2851 | 0.2718 | 1.17 | 0.0235 | 0.9695 |
|              |        | BCF<sub>W</sub> | 1402.44 | 4050.17 | 1946.31 | 10,419.69 | 2280.19 | 352.68 | 1216.42 |
|              | a      | P     | 10.40 | 0.7948 | 3.98 | 11.19 | 59.70 | 1106.74 | 220.01 |
|              |        | BCF<sub>B</sub> | 0.5373 | 0.5637 | 0.0665 | 0.1115 | 0.9112 | 0.8570 | 7.63 |
|              |        | BCF<sub>W</sub> | 1830.70 | 3773.95 | 1502.36 | 8345.79 | 2267.77 | 2060.09 | 1018.47 |
| Rybnia       | s      | P     | 8.12 | 0.7896 | 5.85 | 14.84 | 67.48 | 670.31 | 136.13 |
|              |        | BCF<sub>B</sub> | 0.7871 | 1.76 | 0.5468 | 0.2702 | 1.25 | 0.0805 | 0.8271 |
|              |        | BCF<sub>W</sub> | 1523.15 | 4205.99 | 3029.93 | 11,317.14 | 792.60 | 1124.01 | 1197.50 |
|              | a      | P     | 8.16 | 0.7172 | 2.89 | 10.09 | 55.41 | 365.65 | 137.14 |
|              |        | BCF<sub>B</sub> | 1.09 | 0.6139 | 0.1091 | 0.1167 | 1.02 | 0.4371 | 8.65 |
|              |        | BCF<sub>W</sub> | 1906.24 | 2753.07 | 1463.51 | 5727.57 | 2388.47 | 279.38 | 539.23 |
| Jaworzynik   | s      | P     | 7.96 | 0.8315 | 5.92 | 16.61 | 70.24 | 270.17 | 148.86 |
|              |        | BCF<sub>B</sub> | 0.6727 | 0.9337 | 0.3613 | 0.3307 | 1.35 | 0.6132 | 1.67 |
|              |        | BCF<sub>W</sub> | 1760.75 | 3752.18 | 2880.87 | 13,096.07 | 3566.47 | 381.96 | 1102.57 |
|              | a      | P     | 10.72 | 0.7510 | 4.91 | 11.41 | 73.74 | 840.96 | 239.53 |
|              |        | BCF<sub>B</sub> | 0.6312 | 0.8346 | 0.1875 | 0.0756 | 0.8429 | 0.5640 | 11.69 |
|              |        | BCF<sub>W</sub> | 2162.08 | 2489.62 | 2193.52 | 7099.72 | 3982.27 | 809.70 | 404.88 |

Table 8. Cont.
### Table 8. Cont.

| Site                     | Season | Index | Cu   | Cd   | Ni   | Pb   | Zn   | Fe   | Mn   |
|--------------------------|--------|-------|------|------|------|------|------|------|------|
| Walimianka               | s      | P     | 7.67 | 0.8641 | 6.97 | 13.46 | 75.83 | 284.44 | 98.98     |
|                          |        | BCF<sub>B</sub> | 0.3631 | 0.6287 | 0.2113 | 0.1269 | 0.7420 | 0.0285 | 1.49     |
|                          |        | BCF<sub>W</sub> | 1980.58 | 5970.66 | 3383.59 | 12,188.28 | 3891.11 | 423.20 | 742.38     |
|                          | a      | P     | 10.98 | 1.83 | 5.91 | 15.99 | 73.81 | 815.24 | 166.56     |
|                          |        | BCF<sub>B</sub> | 0.2889 | 1.99 | 0.2231 | 0.1940 | 0.9626 | 0.6319 | 6.10     |
|                          |        | BCF<sub>W</sub> | 1887.30 | 2857.64 | 3249.24 | 9677.82 | 3491.98 | 1262.78 | 623.38     |
| Bystrzyca mouth to the reservoir | s      | P     | 11.12 | 1.06 | 7.52 | 17.54 | 87.69 | 1306.91 | 328.75     |
|                          |        | BCF<sub>B</sub> | 1.22 | 2.32 | 0.5628 | 0.2878 | 1.49 | 0.1568 | 1.21     |
|                          |        | BCF<sub>W</sub> | 2167.43 | 4611.22 | 2968.02 | 11,986.16 | 3362.71 | 1340.07 | 1335.52     |
|                          | a      | P     | 8.71 | 0.8433 | 6.22 | 16.82 | 67.89 | 1276.47 | 185.99     |
|                          |        | BCF<sub>B</sub> | 0.1162 | 0.3019 | 0.0727 | 0.0278 | 0.1665 | 0.5068 | 8.79     |
|                          |        | BCF<sub>W</sub> | 1330.72 | 1862.86 | 2825.19 | 9864.57 | 3227.67 | 1545.73 | 769.14     |

s—spring, a—autumn, P—metal content in the plant; BCF<sub>B</sub>—metals bioaccumulation factor—bottom sediment; BCF<sub>W</sub>—metals bioaccumulation factor—water

### Table 9. Metals and metal bioaccumulation factors relative to water (BCF<sub>W</sub>) and bottom sediment (BCF<sub>B</sub>) in reed canary grass in successive tributaries of the Nysa Szalona River in spring and autumn (mean values).

| Site                         | Season | Index | Cu   | Cd   | Ni   | Pb   | Zn   | Fe   | Mn   |
|------------------------------|--------|-------|------|------|------|------|------|------|------|
| Nysa Szalona below springs   | s      | P     | 36.51 | 1.89 | 3.82 | 19.26 | 38.37 | 174.43 | 188.77     |
|                              |        | BCF<sub>B</sub> | 0.8205 | 1.75 | 0.0801 | 0.5376 | 0.3614 | 0.0090 | 0.8276     |
|                              |        | BCF<sub>W</sub> | 9424.22 | 2944.20 | 1506.79 | 6159.87 | 1516.03 | 424.19 | 1488.53     |
|                              | a      | P     | 8.46 | 0.7734 | 6.81 | 24.06 | 51.82 | 557.73 | 557.73 | 170.16     |
|                              |        | BCF<sub>B</sub> | 0.2056 | 0.5259 | 0.1186 | 0.5208 | 0.2518 | 0.0363 | 0.9306     |
|                              |        | BCF<sub>W</sub> | 658.18 | 1164.54 | 1902.50 | 10,484.17 | 2271.94 | 519.73 | 1058.16     |
| Kocik                        | s      | P     | 48.63 | 2.95 | 5.66 | 34.43 | 35.16 | 105.77 | 131.99     |
|                              |        | BCF<sub>B</sub> | 1.50 | 2.98 | 0.1781 | 1.03 | 0.5112 | 0.0081 | 1.11     |
|                              |        | BCF<sub>W</sub> | 8740.48 | 3175.67 | 561.45 | 8032.97 | 900.15 | 287.88 | 1241.85     |
|                              | a      | P     | 7.00 | 0.7227 | 7.07 | 14.51 | 50.96 | 502.20 | 502.20 | 99.92     |
|                              |        | BCF<sub>B</sub> | 0.1691 | 0.4732 | 0.0901 | 0.1804 | 0.2915 | 0.0122 | 0.6130     |
|                              |        | BCF<sub>W</sub> | 892.75 | 1649.43 | 2728.70 | 8615.97 | 3713.70 | 495.16 | 604.44     |
| Ochodnik                     | s      | P     | 32.25 | 1.84 | 3.64 | 13.77 | 26.05 | 103.18 | 77.94     |
|                              |        | BCF<sub>B</sub> | 1.22 | 2.13 | 0.1099 | 0.7081 | 0.4611 | 0.0059 | 0.5096     |
|                              |        | BCF<sub>W</sub> | 10,944.88 | 1786.49 | 1445.85 | 4625.74 | 671.58 | 465.41 | 663.85     |
|                              | a      | P     | 8.37 | 0.8827 | 6.87 | 13.03 | 38.57 | 73.12 | 489.52     |
|                              |        | BCF<sub>B</sub> | 0.2151 | 0.4929 | 0.0668 | 0.2247 | 0.2314 | 0.0251 | 0.4797     |
|                              |        | BCF<sub>W</sub> | 808.44 | 1162.74 | 2012.21 | 6181.79 | 2112.21 | 468.08 | 135.31     |

s—spring, a—autumn, P—metal content in the plant; BCF<sub>B</sub>—metals bioaccumulation factor—bottom sediment; BCF<sub>W</sub>—metals bioaccumulation factor—water
### Table 9. Cont.

| Site          | Season | Index | Cu   | Cd   | Ni   | Pb   | Zn   | Fe   | Mn   |
|---------------|--------|-------|------|------|------|------|------|------|------|
| Sadówka      | s      |       | 31.44 | 1.66 | 5.28 | 26.95 | 26.86 | 153.60 | 91.67 |
|               | a      |       | 2.11  | 5.30 | 0.2184 | 1.58 | 0.4366 | 0.0083 | 0.5537 |
|               |        | BCF_W | 4299.59 | 1624.59 | 1373.36 | 6138.93 | 464.15 | 627.35 | 918.26 |
|               |        | P     | 9.59 | 9.681 | 7.35 | 13.21 | 41.98 | 957.77 | 139.19 |
|               |        | BCF_B | 0.3769 | 0.8065 | 0.1164 | 0.4682 | 0.4419 | 0.0547 | 0.8468 |
|               |        | BCF_W | 919.14 | 1768.17 | 2226.14 | 6942.56 | 2519.24 | 894.02 | 708.54 |
| Czyściel      | s      |       | 35.16 | 2.76 | 6.26 | 23.75 | 52.77 | 61.31 | 1016.12 | 157.43 |
|               | a      |       | 1.36  | 6.56 | 0.2214 | 1.38 | 0.7647 | 0.0703 | 0.1023 |
|               |        | BCF_W | 6166.11 | 2966.49 | 911.38 | 6187.23 | 1241.38 | 872.83 | 5861.57 |
|               |        | P     | 11.02 | 0.99 | 8.06 | 13.80 | 61.31 | 1016.12 | 157.43 |
|               |        | BCF_B | 0.5367 | 0.8924 | 0.1164 | 0.4682 | 0.4419 | 0.0547 | 0.8468 |
|               |        | BCF_W | 1366.99 | 1329.11 | 1580.58 | 6631.28 | 3562.12 | 1247.23 | 1275.31 |
| Radynia       | s      |       | 34.50 | 3.28 | 5.45 | 19.28 | 34.61 | 125.41 | 46.58 |
|               | a      |       | 0.9045 | 5.63 | 0.2554 | 1.63 | 0.6688 | 0.0135 | 0.9791 |
|               |        | BCF_W | 7748.10 | 1875.02 | 1887.84 | 7592.92 | 3481.09 | 1145.74 | 6038.72 |
|               |        | P     | 11.98 | 1.048 | 8.59 | 17.59 | 66.74 | 146.59 | 596.40 |
|               |        | BCF_B | 0.5168 | 0.9022 | 0.3013 | 0.6484 | 0.8925 | 0.0709 | 1.43 |
|               |        | BCF_W | 884.26 | 1759.90 | 1887.84 | 7592.92 | 3481.09 | 1145.74 | 6038.72 |
| Nysa Mała     | s      |       | 50.77 | 2.51 | 4.89 | 22.54 | 35.12 | 125.41 | 183.54 |
|               | a      |       | 2.20  | 3.12 | 0.1716 | 1.30 | 0.6995 | 0.0205 | 1.32 |
|               |        | BCF_W | 13,980.43 | 3764.47 | 721.65 | 7320.76 | 872.36 | 589.14 | 2047.10 |
|               |        | P     | 6.68  | 1.08 | 8.29 | 14.28 | 52.31 | 376.44 | 143.59 |
|               |        | BCF_B | 0.2606 | 0.9022 | 0.3013 | 0.6484 | 0.8925 | 0.0709 | 1.43 |
|               |        | BCF_W | 966.50 | 3402.81 | 2314.30 | 6954.34 | 2696.28 | 1082.02 | 1066.88 |
| Puszówka      | s      |       | 59.47 | 3.09 | 5.24 | 24.67 | 37.66 | 260.57 | 162.69 |
|               | a      |       | 1.64  | 3.05 | 0.1348 | 1.16 | 0.8649 | 0.0157 | 1.12 |
|               |        | BCF_W | 6938.02 | 3324.72 | 694.19 | 6799.53 | 927.84 | 216.39 | 939.19 |
|               |        | P     | 10.03 | 0.8572 | 7.84 | 15.65 | 54.17 | 627.12 | 107.87 |
|               |        | BCF_B | 0.4917 | 0.6968 | 0.1112 | 0.3349 | 0.3291 | 0.0557 | 0.9026 |
|               |        | BCF_W | 705.87 | 3181.92 | 2964.19 | 7768.64 | 2822.79 | 1820.98 | 1051.78 |
| Jawornik      | s      |       | 41.91 | 2.29 | 3.29 | 21.25 | 27.93 | 172.52 | 140.59 |
|               | a      |       | 1.56  | 4.89 | 0.1133 | 0.4834 | 0.5384 | 0.0095 | 0.9221 |
|               |        | BCF_W | 3826.07 | 1605.25 | 346.08 | 5896.69 | 598.35 | 43.05 | 888.79 |
|               |        | P     | 9.11  | 0.8470 | 9.49 | 22.20 | 65.65 | 525.28 | 111.21 |
|               |        | BCF_B | 0.4925 | 0.5718 | 0.1328 | 0.4469 | 0.7497 | 0.0381 | 0.6697 |
|               |        | BCF_W | 763.88 | 3043.43 | 3648.54 | 9100.88 | 5875.10 | 1562.28 | 5067.93 |
Table 9. Cont.

| Site                        | Season | Index | Cu  | Cd  | Ni   | Pb   | Zn   | Fe   | Mn   |
|-----------------------------|--------|-------|-----|-----|------|------|------|------|------|
| Księginka                    | s      | P     | 42.96 | 1.84 | 5.09 | 17.22 | 24.85 | 155.77 | 169.68 |
|                             |        | BCF_B | 2.06  | 2.03  | 0.1733 | 0.5313 | 0.5833 | 0.0102 | 1.40  |
|                             |        | BCF_W | 4630.89 | 1138.85 | 589.89 | 7565.16 | 471.94 | 182.38 | 1002.67 |
|                             | a      | P     | 10.19 | 0.8530 | 12.48 | 21.93 | 56.08 | 972.19 | 153.43 |
|                             |        | BCF_B | 0.3443 | 0.4470 | 0.2115 | 0.5538 | 0.6312 | 0.0815 | 1.24  |
|                             |        | BCF_W | 905.80 | 1368.26 | 3838.03 | 13,660.08 | 3746.98 | 4306.72 | 1407.27 |
| Starucha                    | s      | P     | 56.91 | 1.43 | 5.02 | 41.06 | 37.91 | 156.50 | 127.29 |
|                             |        | BCF_B | 2.88  | 5.00  | 0.1689 | 0.6327 | 0.9066 | 0.0065 | 0.9767 |
|                             |        | BCF_W | 16,282.90 | 1753.65 | 451.39 | 16,076.21 | 1212.12 | 78.55 | 577.34 |
|                             | a      | P     | 15.87 | 1.12 | 9.50 | 30.96 | 52.55 | 613.21 | 195.21 |
|                             |        | BCF_B | 0.3554 | 0.7379 | 0.1420 | 0.5620 | 0.6312 | 0.0815 | 1.24  |
|                             |        | BCF_W | 927.63 | 2710.57 | 3201.54 | 13,961.11 | 3230.41 | 942.94 | 207.72 |
| Rowiec                      | s      | P     | 70.94 | 2.25 | 5.84 | 21.23 | 41.04 | 242.25 | 136.60 |
|                             |        | BCF_B | 3.66  | 2.01  | 0.1996 | 0.7787 | 0.5844 | 0.0239 | 0.4243 |
|                             |        | BCF_W | 20,728.49 | 2710.57 | 1690.98 | 11,299.22 | 931.04 | 185.35 | 1014.34 |
|                             | a      | P     | 12.09 | 1.02 | 9.62 | 28.89 | 41.04 | 242.25 | 136.60 |
|                             |        | BCF_B | 0.2083 | 0.6039 | 0.1216 | 0.3819 | 0.1484 | 0.0419 | 0.6544 |
|                             |        | BCF_W | 927.63 | 3409.07 | 2398.85 | 16,850.92 | 2001.01 | 868.68 | 1009.96 |
| Męcinka                     | s      | P     | 105.33 | 2.34 | 4.17 | 21.97 | 32.13 | 188.22 | 260.75 |
|                             |        | BCF_B | 2.38  | 2.24  | 0.1056 | 0.4697 | 0.3827 | 0.0098 | 0.8907 |
|                             |        | BCF_W | 19,305.28 | 3060.20 | 312.06 | 7877.71 | 1154.99 | 319.38 | 1963.53 |
|                             | a      | P     | 8.99  | 0.9406 | 9.28  | 28.89 | 57.52 | 539.16 | 120.20 |
|                             |        | BCF_B | 0.1519 | 0.3449 | 0.0827 | 0.3536 | 0.3018 | 0.0212 | 0.6379 |
|                             |        | BCF_W | 705.49 | 2702.23 | 2699.49 | 13,665.86 | 2894.48 | 1043.47 | 988.42 |
| Nysa Szalona mouth to the reservoir | s      | P     | 79.27 | 2.75 | 4.39 | 26.56 | 46.56 | 154.83 | 240.61 |
|                             |        | BCF_B | 2.3199 | 2.9099 | 0.1319 | 0.5313 | 0.6728 | 0.0085 | 0.7831 |
|                             |        | BCF_W | 14,478.94 | 2848.01 | 335.22 | 11,093.39 | 1278.15 | 185.05 | 1602.91 |
|                             | a      | P     | 10.14 | 1.17 | 10.03 | 30.24 | 65.98 | 510.58 | 367.16 |
|                             |        | BCF_B | 0.2291 | 0.6019 | 0.1083 | 0.3412 | 0.3737 | 0.0301 | 2.0469 |
|                             |        | BCF_W | 1162.78 | 1955.63 | 2980.21 | 12,845.75 | 3442.69 | 892.13 | 3163.58 |

s—spring, a—autumn, P—metal content in the plant; BCF_B—metals bioaccumulation factor—bottom sediment; BCF_W—metals bioaccumulation factor—water

Furthermore, differences between the spring and autumn seasons are noticeable. Spring was the most differentiated season with respect to the studied parameters (Figure 11).
3.3. Metals in Tributaries of Major Rivers

The analysis of metal contents in plants taken from successive tributaries of the three main rivers shows that in the Strzegomka River, the level of Cu, Ni, Cd, Fe, Mn increased with the river course and in the middle part the content of these metals was the highest. For lead, no major changes were observed in the whole river, and the range of values was 7.12 to 9.58 mgPb·kg⁻¹ (Table 7). For zinc, values decreased with the river course from 89.90 mgZn·kg⁻¹ to 63.46 mgZn·kg⁻¹ in spring, and from 56.49 mgZn·kg⁻¹ to 47.89 mgZn·kg⁻¹ in autumn.

In the Bystrzyca River, copper, nickel, and cadmium levels increased downstream (Table 8). In the case of zinc, the upper and lowland tributaries contributed higher amounts than the midstream rivers. For iron and manganese, decreasing values were observed with the direction of water flow in the river.

In the case of the Nysa Szalona River, the amount of copper and lead in plant samples increased steadily with successive tributaries (Table 9). It was also observed that the midstream rivers contributed higher amounts of cadmium, zinc and manganese, and lower amounts of iron. Nickel remained at an even level in all tributaries.

Two groups of elements clearly emerge from the study. The first one includes Pb, Cu and Cd, and they turned out to be statistically highly correlated (Figure 12). The second group of metals includes Zn, Ni, Fe, Mn which are a group of elements correlated with each other. More detailed values of correlations are given in Table 10.
Figure 12. Ordination of the 29 study sites by PCCA based on concentrations of elements in plants and water (pH) in all investigated rivers.

Table 10. Spearman’s correlation of metal content in reed canary grass and water reaction, study site, season and year. Differences statistically significant at $p \leq 0.05$ marked with red.

|   | Ni  | Cd  | Pb  | Mn  | Zn  | Fe  | pH  | site  | river  | season | year  | Cu  | Ni  | Cd  | Pb  | Zn  | Mn  | Fe  | pH  | site | river | season |
|---|-----|-----|-----|-----|-----|-----|-----|-------|--------|--------|-------|-----|-----|-----|-----|-----|-----|-----|-----|-------|--------|--------|
| Ni | 0.13|     |     |     |     |     |     |       |        |        |       |     |     |     |     |     |     |     |       |        |        |
| Cd | 0.34| 0.22|     |     |     |     |     |       |        |        |       |     |     |     |     |     |     |     |       |        |        |
| Pb | 0.23| 0.36| 0.45|     |     |     |     |       |        |        |       |     |     |     |     |     |     |     |       |        |        |
| Mn | 0.30| 0.19| 0.25| 0.26| 0.26|     |     |       |        |        |       |     |     |     |     |     |     |     |       |        |        |
| Zn | 0.05| 0.30| 0.03| 0.04|     |     |     |       |        |        |       |     |     |     |     |     |     |     |       |        |        |
| Fe | −0.03| 0.39| −0.06| −0.08| 0.56| 0.41|     |       |        |        |       |     |     |     |     |     |     |     |       |        |        |
| pH | 0.05| 0.00| −0.27| −0.31| −0.10| −0.13| 0.05|       |        |        |       |     |     |     |     |     |     |     |       |        |        |
| site | 0.03| 0.19| 0.18| 0.29| −0.13| −0.01| −0.10| −0.07|       |        |       |     |     |     |     |     |     |     |       |        |        |
| river | 0.31| 0.15| 0.04| −0.03| −0.14| −0.10| −0.10| 0.41| −0.13|       |       |     |     |     |     |     |     |     |       |        |        |
| season | −0.06| 0.24| −0.10| −0.09| 0.10| 0.08| 0.33| 0.25| 0.00| 0.00|       |     |     |     |     |     |     |     |       |        |        |
| year | −0.14| 0.01| −0.21| −0.19| −0.04| −0.19| 0.14| 0.37| 0.00| 0.00| 0.00|     |     |     |     |     |     |     |       |        |        |

The investigated river ecosystem covers a considerable area of the south-western part of Poland. In this area, besides groundwater, rivers as surface waters are the main source of drinking water supply for the population. The content of metals in plants growing in the riverbeds which supply the reservoirs from which drinking water is obtained suggests that they do not pose a threat to human life. The level of metals in hydromacrophytes is within the average limits for these types of waters in this climatic zone. This is confirmed by the results of the studies by the authors cited above [2,4,17,18,35,39,54]. Also, the concentrations of metals in river water recorded throughout the four-year study cycle are low enough to meet the criteria for water extracted by water production plants for water production [57,58]. If the natural environment continues to be so stable, and there are no
changes in the reaction of water and bottom sediments, it can be assumed that the current level of metals in water and plants will not pose a threat to human health in this area in the future.

3.4. Metal Pollution Index (MPI) and Enrichment Factor (EF)

The metal pollution index (MPI) of aquatic plants was used to compare the metal content of samples from different sites [29]. The general pattern of MPI in aquatic plants was arranged in a series B < S < NS, and the same pattern was found for water, however a slightly different order occurred for sediments: S < B < NS (Table 11) [17,18]. During the four-year cycle of the study, higher MPI values were recorded in 2016 and 2018 than in 2015 and 2017 (Table 12).

Table 11. Metal pollution index (MPI) of aquatic plants, bottom sediments and water.

|                | Nysa Szalona | Bystrzyca | Strzegomka |
|----------------|--------------|-----------|------------|
| Plant          | 41.87        | 31.81     | 36.40      |
| Sediment       | 277.26       | 189.41    | 50.46      |
| Water          | 0.0903       | 0.0396    | 0.0826     |
| pollution degree| high        | high      | high       |

Table 12. Metal pollution index (MPI) of aquatic plants—mouth, sources in subsequent years.

|                | Nysa Szalona | Bystrzyca | Strzegomka |
|----------------|--------------|-----------|------------|
| 2015 Source    | 16.71        | 15.70     | 17.09      |
| Mouth          | 28.90        | 22.54     | 20.72      |
| pollution degree| moderate     | high      | moderate   |
| 2016 Source    | 15.87        | 26.06     | 21.21      |
| Mouth          | 18.07        | 26.85     | 27.44      |
| pollution degree| moderate     | high      | high       |
| 2017 Source    | 18.22        | 44.95     | 53.29      |
| Mouth          | 24.89        | 49.74     | 38.08      |
| pollution degree| moderate     | high      | very high  |
| 2018 Source    | 25.48        | 12.13     | 10.24      |
| Mouth          | 22.00        | 8.63      | 14.39      |
| pollution degree| high         | moderate  | moderate   |

These values classify the studied material at high pollution degree in all rivers. Against this background, previously published data for sediment reached the highest and very high grades [18]. In the case of the MPI for water, no effect of pollution was found [17]. With this comparison, it can be seen that it is only when metal levels in sediments and plants are studied that the accumulation of metals in the environment becomes apparent. Hence, conducting a comprehensive study is justified. In the comparison of the two extreme sites: source–mouth, the predominance of higher values at the reservoir mouth in the first three years of the study is evident, indicating the origin of these metals from the catchment. On the other hand, in the last year (2018) higher MPI values were found at the sources in the Nysa Szalona and Bystrzyca Rivers (Table 12).

The enrichment factor (EF) calculated for all plant samples reached the lowest values for nickel and the highest values for lead and manganese (Tables 13–15). The series of increasing values were as follows: Bystrzyca—Ni < Cd < Fe < Cu < Zn < Mn < Pb, Nysa Szalona—Ni < Fe < Zn < Cd < Mn < Cu < Pb, Strzegomka—Ni < Cd < Fe < Zn < Cu < Pb < Mn. For all studied plants in each of the three rivers, the values were definitely higher in spring than in autumn.
Table 13. Enrichment factor (EF) in reed canary grass from the Bystrzyca River.

|                         | Cu   | Cd   | Ni   | Pb   | Zn   | Fe   | Mn   |
|-------------------------|------|------|------|------|------|------|------|
| Bystrzyca and tributaries |      |      |      |      |      |      |      |
| whole                   | 12.86| 7.03 | 4.33 | 76.91| 14.41| 7.32 | 49.51|
| spring                  | 208.43| 115.48| 79.68| 1413.89| 265.62| 362.01| 185.72|
| autumn                  | 6.79 | 3.66 | 1.99 | 35.44| 6.62 | 8.17 | 16.73|
| tributaries             |      |      |      |      |      |      |      |
| whole                   | 11.46| 6.11 | 3.75 | 67.91| 12.74| 5.59 | 37.47|
| spring                  | 330.61| 129.76| 82.69| 793.15| 286.31| 868.54| 184.04|
| autumn                  | 9.73 | 3.34 | 2.91 | 24.49| 5.71 | 12.19| 5.74 |
| Bystrzyca below sources |      |      |      |      |      |      |      |
| whole                   | 14.25| 11.64| 5.55 | 93.92| 20.11| 17.53| 92.74|
| spring                  | 286.54| 296.67| 114.86| 2335.42| 475.51| 450.83| 328.71|
| autumn                  | 8.14 | 5.21 | 3.10 | 43.72| 9.91 | 41.83| 25.36|
| Bystrzyca outlet to the reservoir |      |      |      |      |      |      |      |
| whole                   | 41.97| 19.32| 15.13| 248.15| 40.73| 128.83| 46.87|
| spring                  | 118.32| 54.20| 41.65| 637.09| 115.46| 327.77| 150.56|
| autumn                  | 22.99| 10.70| 8.55 | 151.62| 22.18| 79.45 | 21.14|

Table 14. Enrichment factor (EF) in reed canary grass from the Nysa Szalona River.

|                         | Cu   | Cd   | Ni   | Pb   | Zn   | Fe   | Mn   |
|-------------------------|------|------|------|------|------|------|------|
| Nysa Szalona and tributaries |      |      |      |      |      |      |      |
| whole                   | 33.42| 8.54 | 3.79 | 81.88| 5.94 | 4.74 | 21.39|
| spring                  | 1440.77| 313.76| 70.28| 2261.97| 122.05| 185.42| 267.61|
| autumn                  | 14.42| 8.46 | 6.54 | 121.20| 9.25 | 15.48| 13.93|
| tributaries             |      |      |      |      |      |      |      |
| whole                   | 31.52| 8.17 | 3.67 | 76.65| 5.54 | 11.66| 7.86 |
| spring                  | 1462.44| 324.74| 74.68| 2356.84| 122.19| 205.29| 278.86|
| autumn                  | 5.42 | 2.39 | 2.37 | 35.07| 3.42 | 8.13 | 2.92 |
| Nysa Szalona below sources |      |      |      |      |      |      |      |
| whole                   | 45.02| 12.80| 5.55 | 148.09| 11.18| 17.28| 15.47|
| spring                  | 1519.64| 378.06| 82.76| 2736.66| 197.64| 171.13| 338.19|
| autumn                  | 8.68 | 3.81 | 3.64 | 84.28| 6.58 | 13.49| 7.52 |
| Nysa Szalona outlet to the reservoir |      |      |      |      |      |      |      |
| whole                   | 52.65| 11.09| 4.42 | 114.20| 8.20 | 9.24 | 15.41|
| spring                  | 1268.06| 211.41| 36.55| 1450.43| 92.17| 58.38| 165.67|
| autumn                  | 6.20 | 3.44 | 3.19 | 63.13| 4.99 | 7.36 | 9.66 |

In the Bystrzyca River, higher values of the enrichment factor EF were found at the site immediately upstream of the reservoir and in the Nysa Szalona River at the site downstream of the springs. In the Strzegomka River, a differentiation was observed: higher values for Cu, Ni, Fe and Mn were recorded downstream of the source, while the remaining metals were observed at the upstream site.

For most samples, Cu and Fe are within the range of moderate values. Lead and manganese reach very high and extremely high values. The remaining metals fall in the values described as significant. This assessment suggests that the amount of metals absorbed by reed canary grass varies. While for the time being there is no concern about the levels of copper and iron, for the rest of the metals a more frequent, regular study should be carried out.
Table 15. Enrichment factor (EF) in reed canary grass from the Strzegomka River.

| Strzegomka and tributaries | Cu  | Cd  | Ni  | Pb  | Zn  | Fe  | Mn  |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|
| whole                     | 14.68 | 5.29 | 4.24 | 36.87 | 10.22 | 6.22 | 66.88 |
| spring                    | 280.40 | 103.53 | 71.49 | 657.66 | 241.13 | 174.87 | 839.28 |
| autumn                    | 8.21 | 2.93 | 2.61 | 21.73 | 4.59 | 7.37 | 17.06 |

| tributaries               | Cu  | Cd  | Ni  | Pb  | Zn  | Fe  | Mn  |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|
| whole                     | 11.30 | 4.13 | 3.13 | 27.82 | 8.04 | 25.48 | 6.49 |
| spring                    | 228.89 | 122.84 | 62.23 | 1148.85 | 216.59 | 230.89 | 458.38 |
| autumn                    | 5.07 | 2.24 | 2.22 | 32.78 | 3.20 | 2.73 | 7.59 |

| Strzegomka below sources  | Cu  | Cd  | Ni  | Pb  | Zn  | Fe  | Mn  |
|---------------------------|-----|-----|-----|-----|-----|-----|-----|
| whole                     | 23.37 | 8.42 | 8.75 | 59.09 | 16.59 | 35.26 | 77.62 |
| spring                    | 17.71 | 120.88 | 93.30 | 771.58 | 316.79 | 270.86 | 1408.89 |
| autumn                    | 364.89 | 5.26 | 6.19 | 37.51 | 7.49 | 37.26 | 28.12 |

| Strzegomka outlet to the reservoir | Cu  | Cd  | Ni  | Pb  | Zn  | Fe  | Mn  |
|-----------------------------------|-----|-----|-----|-----|-----|-----|-----|
| whole                             | 13.01 | 9.96 | 7.13 | 75.06 | 18.38 | 19.43 | 69.55 |
| spring                            | 206.01 | 70.25 | 55.38 | 493.22 | 172.38 | 143.57 | 660.60 |
| autumn                            | 16.49 | 5.86 | 3.79 | 46.21 | 7.76 | 28.76 | 10.86 |

4. Conclusions

A four-year study of reed canary grass in rivers of southwestern Poland ranked metal levels as follows: Nysa Szalona and Strzegomka: Cd < Ni < Pb < Cu < Zn < Mn < Fe, and Bystrzyca: Cd < Ni < Cu < Pb < Zn < Mn < Fe. Throughout the study period, the lowest values of metals in plants were recorded in 2015 and 2018, and the highest in 2017.

The general picture of MPI in aquatic plants is arranged in the series Bystrzyca < Strzegomka < Nysa Szalona. These values classify the studied material at a high level of pollution in all rivers. In the comparison of two extreme sites, i.e., source–mouth, higher values are found at the mouth of the reservoir, which suggests that metals move with the water current and accumulate more with the direction of the river flow, which is most likely a consequence of the influence of the catchment area as the source of metals.

The series of enrichment factor (EF) values were as follows: Bystrzyca—Ni < Cd < Fe < Cu < Zn < Mn < Pb, Nysa Szalona—Ni < Fe < Zn < Cd < Mn < Cu < Pb, Strzegomka—Ni < Cd < Fe < Zn < Cu < Pb < Mn. For all the samples studied, the values found in spring were much higher than in autumn, which would indicate the great importance of conducting research in that area.

Bioaccumulation of metals determined relative to bottom sediments was highest in 2017 and lowest in 2018, while bioaccumulation relative to water was highest in 2018 and lowest in 2016.

The four-year study found that the metal content in reed canary grass was mostly within the range of the mean values presented in literature data from moderately polluted areas. Also, no significant deviation was found from levels that have been recorded for the same rivers for more than two decades.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijerph19137779/s1, Table S1. Characteristics of the rivers under examination [13–15,19,20].

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