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Assessment of the condition of Biebrza river aquatic environment with the use of *Phragmites australis (Cav.) Trin. ex Steud* (Poland)

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ABSTRACT

The purpose of the work was to determine the content of Ni, Co, Pb, Zn, Cu, Cr, Cd, Fe, and Mn in. *Phragmites australis (Cav.) Trin. ex Steud* (root, stem, leaf) and bottom sediments of Biebrza river, and also to investigate whether *Phragmites australis* may have potential application in bio-monitoring of the aquatic environment. The research concerned the identification of factors and processes governing the behavior of selected metals in the river. The metals were determined by means of atomic absorption spectrometry. Results showed that the metal content in various *Phragmites australis* organs varied, and the largest content occurred in the roots. Limited mobility and translocation of metals present in the plant make it a good species for the phyto-stabilization of bottom sediments, in particular in the case of Fe. Statistical models factor analysis (CA) allowed identifying the main routes of metals transport from the Biebrza river catchment. These are canals, streams and ditches draining various areas of use.

Keywords: Metals; *Phragmites australis*; Bottom sediments; Rivers; Contamination sources

1. Introduction

Intensified development of the economy has a negative impact on the environment and especially threatens natural water ecosystems [1]. A variety of contaminants, including heavy metals, get into the surface waters [2]. Heavy metals occurring in rivers come from both natural and anthropogenic sources [3]. In the face of intense human activity, natural sources of metals from leaching and weathering of rocks in the environment can be usually neglected. However, anthropogenic sources are of great importance. They are mainly related to the discharge of industrial, mine and municipal sewage, atmospheric pollution, transport, runoff from areas used for agriculture and intensive fertilization [4–6]. In addition, heavy metals are harmful to the environment due to their properties, because they are toxic and not biodegradable [7]. The degree of rivers contamination with heavy metals can be determined based on bottom sediments and aquatic plant studies [8,9]. River sediments and aquatic plants are an integral part of surface waters, mainly due to active participation in the circulation of elements. There is a large dependence between the content of metals in river sediments and macrophytes and their concentration in water [10]. Contaminants in bottom sediments can be collected by rooted aquatic plants. According to Marchand et al. [11], rooted macrophytes have a high capacity to accumulate heavy metals from sediments. Their metal accumulation features make them interesting research objects. They are a local bio-filter that easily reaches the place of contamination and absorbs it [12]. The heavy metal accumulation process in macrophytes is complex. It depends on biotic and abiotic factors, among others, from temperature, redox potential, pH, amount and form of water-soluble ions, as well as plant species and types of elements, as well as

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their interactions [13]. Macrophytes take, move, accumulate and/or decompose contaminants through various metabolic changes. Water plants are able to release metals during the decomposition of organic matter (MO) and then metals are transported to organisms with higher trophic levels [14,15]. Due to their constant contact with water and bottom sediments, macrophytes have been used for many years as a biological indicator material [16,17] and used in bio-monitoring of the aquatic environment [18–20]. The subject of this work is to test the metal content in the aquatic environment of the Biebrza river. This area is slightly transformed by man, there are no mines, heavy industry, large agglomerations, and population density is still small. The presence of forests, wetlands, peatlands, and a clean environment, make this area a mainstay for many species of plants and animals that are often rare both on the national and European scale. Due to its natural values, the Biebrza river catchment was protected by the creation of a national park. The significance of the park is even greater because, at present, only half of the existing wetlands remained in the world [21]. The Biebrza National Park is presented as a model of an almost entirely natural wetland area of Europe. The outstanding natural value of this region has contributed to the study of the Biebrza river ecosystem. Achieving an appropriate quality of the Biebrza river aquatic environment will enable maintaining the greatest possible biodiversity of the aquatic and water-land ecosystem and preventing their degradation as a result of water pollution. It may also be reflected in finding a golden mean between economic development and the needs of the population and the protection of natural values, that is, through the so-called sustainable development. The objectives of the study were as follows: (1) determination of the contents of Ni, Co, Pb, Zn, Cu, Cr, Cd, Fe and Mn in *Phragmites australis (Cav.) Trin. ex Steud* (root, stem, leaf) and bottom sediments of Biebrza river and also to investigate whether *Phragmites australis (Cav.) Trin. ex Steud* may have potential application in biomonitoring of aquatic environment, (2) identifying similarities or differences between sampling sites, (3) impact assessment and identification of metal sources based on river sediments and plant material analysis, (4) obtained results will form the basis for establishing an ecological monitoring system for the natural area of Biebrza river catchment. A special role, in this case, is played by macrophytes due to their natural abilities to remove chemical contaminants from the aquatic environment.

2. Methods

2.1. Study area

Biebrza River is a right-bank tributary of Narew river, 155.3 km long, of which 152.5 km of the river is within the borders of the Biebrza National Park. The area of the river catchment is 7051.2 km^2. Biebrza River is a typical lowland river with low falls. The channel of the river strongly meanders creating numerous bends and oxbow lakes. It is the most meandering river in Poland. The width of the bed is from a few meters in the initial course of the river to a dozen or so near the estuary. The Biebrza river catchment is characterized by a large uneven distribution of tributaries, the right-bank catchment constitutes 75.5% of the total tributaries, and the left-bank basin is only 24.5%. Right-bank tributaries are Niedźwiedzica, Lebiedzianka, Netta and Augustowski Canal, Kopytkówka, Ełk and Jegrznia, Dybła, Klimaszewnica, and Wissa. The left-bank tributaries of Biebrza river are Nurka, Sidra, Kamienna, Brzozówka, Krzeczówka, Biebła, and Kosódka. The landscape of the river valley is characterized by a high level of naturalness. Within Biebrza river valley, there is the largest in Poland (about 100,000 ha), as well as one of the largest, peat bog complex in Europe with fragments of raised and transitional bogs, the mineral plateau of the marshland hornbeam, as well as oxbow lakes and natural river meanders [22]. Due to its high natural values, the Biebrza river catchment was covered by the highest form of protection through the creation of a national park in its area, that in 1995 was included in the list of RAMSAR conventions, that is, wetland areas of international importance. The climate in the studied area is characterized by long winters, short pre-spring period, relatively short vegetation, high air humidity (annual average of 80%), average annual air temperature from 4.8°C to 8.3°C and frequent mists. It is also characterized by relatively high heavy rainfalls of 600–700 mm y^{-1} [23]. Regional policy aimed at sustainable development of industry, taking into account the preservation of the uniqueness of the natural environment, also confirms the unique character of the studied area. The main sources of pollution in the Biebrza river catchment result from the development and functioning of larger settlement units located within the catchment. The quality of the aquatic environment of the Biebrza river is affected by sewage treatment plants, lack or incomplete efficiency of the sewerage network, small industry (wood, meat, food), agriculture (fertilization and plant protection), motor vehicle traffic.

2.2. Sampling and preparation of samples

Samples of bottom sediments and *Phragmites australis (Cav.) Trin. ex Steud* (leaves, stems, and roots) were collected in August 2018 from 11 measuring points (source of the river, Lipsk, Ostrów, Sztabin, Jagłowo, Polkowo, Dolistowo, Goniądz, Osowiec, Brzostowo, and Rutkowskie) on Biebrza river (Fig. 1).

The selection of measuring points was dependent on the spatial distribution of pollution sources in the Biebrza river catchment. Bottom sediment was collected in the boundary zone from the upper layer, where deposition of suspended material and accumulation of heavy metals occurs [24]. A dozen individual samples of bottom sediments were collected at a depth of 5–10 cm below the water surface at each designated measurement point. After mixing the test material, a representative sample of approximately 1,000 g was obtained [25]. The plant material was taken from the same places as the bottom sediments. Macrophyte research samples were created from the combination of several individual plant samples. *Phragmites australis (Cav.) Trin. ex Steud* is a cosmopolitan species that is widespread throughout the world. It creates compact and dense clumps. It is the largest herb in the Polish flora. It is a typical swamp and aquatic plant. It is very vital and grows very quickly. It also grows in waters strongly contaminated with municipal sewage.

Fig. 1. Sampling points on the Biebrza river.

2.3. Analytical procedures

Bottom sediment samples were dried to "air-dry condition" and stored until testing. Before proceeding with chemical analyzes, the bottom sediment samples were dried at 40°C and sieved through a 0.2 mm sieve. Bottom sediments were mineralized with hydrochloric and nitric acid in a volume ratio of 3:1 in a closed CEM Corporation (USA) microwave system. All determinations were carried out in triplicate. The samples, after filtration, were quantitatively transferred to 50 ml graduated flasks. The content of heavy metals was determined by flame atomic absorption spectrometry on the atomic absorption spectroscopy (AAS) iCE™ 3500 Thermo Scientific spectrometer (UK and USA). Results of sediment analyzes were verified using certified reference material for sediments NCS DC 73317a. Calculated measurement error did not exceed 5% of the certified value. The reaction of bottom sediments was determined by potentiometric method. Organic substance content was determined based on the weight difference of samples before and after combustion at 450°C. The pH of sediments in the water was tested potentiometrically.

The plants transported to the laboratory were washed with running water and distilled water, then dried at 80°C [26]. Dried roots, stems and leaves were homogenized and digested with hydrochloric and nitric acid in 3:1 volume ratio in a closed CEM microwave system. Content of heavy metals was determined by flame atomic absorption spectrometry on the AAS iCE™ 3500 Thermo Scientific spectrometer (UK and USA). The measurement error of the analysis was determined by comparing the obtained results with characteristics of the grass mixture - European Reference Materials (ERM®) - CD281 and strawberry leaves - LGC7162. Calculated measurement error did not exceed 5% of the certified value.

Obtained results of investigated metals content were given in relation to dry mass of plants and compared with literature data also referring to dry matter of plants. The physiological norm of metal content for plants is given according to data provided by Kabata-Pendias and Pendias [27], Markert [28]. In the analysis of plant results the bioconcentration coefficient expressed as the ratio of metal content in the plant root to metal content in bottom sediments was calculated. The translocation coefficient was also calculated as a quotient of the content of the examined metal in roots and stems as well as in roots and leaves of the examined macrophytes.

2.4. Assessment of bottom sediments pollution degree

Obtained results of tested metals contents (Ni, Co, Pb, Zn, Cu, Cr, Cd, Fe, and Mn) were given in relation to air dry sediments and compared with literature data. To assess the degree of heavy metal contamination of sediments, the proposed classification of water sediments in Poland was used [24] and the contents of investigated metals were compared to the geochemical background proposed by Turekian and Wedepohl [29]. To assess the quality of bottom sediments of Biebrza river, the degree of sediment pollution was also used, using the geochemical index (I_{geo}).

Geochemical index (I_{geo}) is defined using the following formula [30]:

$$I_{geo} = \log_2\left(\frac{C_m}{1,5\text{GM}}\right) \tag{1}$$

where C_m is the content of analyzed metal (mg kg^{-1}), GM is the geochemical background (mg kg^{-1}).

The I_{geo} values are divided into seven classes, that is, non-polluted sediment class 0 ($I_{geo} \leq 0$), poorly polluted sediment class 1 ($0 < I_{geo} < 1$), moderately contaminated sediment class 2 ($1 < I_{geo} < 2$), averagely contaminated sediment class 3 ($2 < I_{geo} < 3$), highly contaminated sediment class 4 ($3 < I_{geo} < 4$), very heavily polluted class 5 ($4 < I_{geo} < 5$), extremely contaminated sediment class 6 ($I_{geo} \geq 5$).

2.5. Statistical analysis

Relations between heavy metal content in plants and sediments were measured by Pearson correlation analysis. The significance of correlations between data sets at $p < 0.05$ was identified using the Pearson correlation coefficient. Recently, a multidimensional statistical approach has become popular to better understand the quality of aquatic environment and ecological status, due to their ability to process large amounts of spatial and temporal data from different monitoring sites. In the scientific literature, various statistical techniques are used for this type of research, including hierarchical cluster analysis (HCA), factor analysis (FA) and discriminant analysis (DA).

HCA and FA were used to investigate possible sources of heavy metals in plants and sediments. In the HCA analysis, the distance between clusters of heavy metal content was measured by the square of the Euclidean distance according to the Ward method. As a rotation method, Varimax with Kaiser normalization was used [31]. To assess the credibility of the FA, the Kaiser-Meyer-Olkin (KMO) measures were used. Multidimensional statistical techniques have been successfully applied to characterize and assess surface water quality and to identify temporal and spatial changes caused by natural and anthropogenic factors in studies conducted in Argentina [32], Bulgaria [33], Pakistan [34], and Japan [35]. Pearson correlation analysis, HCA and FA were performed using the Statistica ver.13.0 for Windows package.

3. Results and discussion

3.1. Metals content in bottom sediments

When analyzing the aquatic environment with respect to metal content, it should be remembered that bottom sediments may be carriers as well as potential sources of pollution [36]. According to Baldantoni et al. [37], the amount of metals in sediments is an indicator of a long-term accumulation of elements in water reservoirs. The content of tested metals (Ni, Co, Pb, Cu, Zn, Fe, Mn, Cr, and Cd) in bottom sediments from 11 measurement points on Biebrza river is presented in Table 1.

In general, the average metal content in river sediments occurred in the following decreasing order Fe > Mn > Zn > Cu > Co > Pb > Ni > Cr > Cd. The highest amounts of Fe and Mn were found in sediments, while the lowest – Cd, and this is largely the result of the geochemical properties of these elements. Biebrza River catchment is an area of wetlands and peat bogs that can be a natural source of Fe and Mn in bottom sediments. In most cases, the geochemical background established by Turekian and Wedephol [29] is used to assess river sediment contamination, and studies have shown that all analyzed metals are at the level of geochemical background, except from Cd (Table 1). In turn, according to the classification used in Poland, the analysis of sediment test results showed the geochemical background exceeded for Co and Cu (Table 1). On the other hand, the average contents of analyzed elements in the bottom sediments of the Biebrza River are much smaller than the average amount of these metals in sediments in Poland [25]. For all tested trace elements (Ni, Co, Pb, Cu, Zn, Fe, Mn, Cr, and Cd), it was shown that 100% of collected bottom sediment samples reached the negative I_{geo} value, thus they can be classified as uncontaminated bottom sediments - class 0 (Table 2).

The pH of bottom sediments was similar to neutral and slightly alkaline, ranging from 7.6 to 8.2 pH. Sediments were characterized by relatively low content of MO, which ranged from 0.2% to 1.3% (Table 1).

3.2. Metal content in *Phragmites australis*

Chemical composition of surface waters is shaped as a result of many processes including, among others, substance exchange in the system of bottom sediment and aquatic plants. Macrophytes play an important role in aquatic ecosystems [15,17,26]. These organisms have a characteristic structure adapted to life in conditions of constant contact with water. They have an extensive system of micronutrient uptake from the environment. They are considered reliable indicators of the quality of the aquatic environment [14,20]. Many authors Bonanno [18], Mazej and Germ [26], Vereecken et al. [38], Srivastava et al. [39], showed that the content of trace elements accumulated by aquatic plants was proportional to their content in the aquatic environment and could help to estimate levels of pollution.

Ranges of mean contents of the studied elements in roots, stems, and leaves of *Phragmites australis* collected on the Biebrza River, are presented in Table 1. Based on the obtained results, it was observed that all tested plants show similar metal absorption capacity. Most metals occur in the roots, which was also confirmed by research performed by Cardwell et al. [14], Aksoy et al. [40], Vardanyan and Ingole [36], Parzych and Cymer [41]. It was shown that the contents of Ni, Pb, Cu, Zn and Mn in the plant material were within the limits of natural contents determined by Kabata-Pendias and Pendias [27] and Markert [28]. In contrast, Co, Cr, and Cd contents in roots and above-ground parts exceeded physiological values (Table 1). The roots of *Phragmites australis*, referring to these elements, have reached a higher level indicating a protective barrier limiting the movement of Co, Cr and Cd from underground organs to above-ground shoots, which is also confirmed by research by Hozhina et al. [42]. According to Baldantoni et al. [37], high content of metals in roots and low in stems and leaves indicates that sediments are the main source of metals and only not much is transferred to above-ground parts. There were also significant Fe contents in *Phragmites australis* (root – 9,153 ± 4,651, stem – 399 ± 521, and leaf – 711 ± 1,119 mg kg^{-1}) and did not fall within the limit values for plants (50–200 mg kg^{-1}). Iron content above 500 mg kg^{-1} is considered to be toxic to plants [43]. Such high contents of this element may prove the cumulative properties of this species in relation to Fe. According to Kabata-Pendias and Pendias [27], Fe belongs to the elements of low mobility in the plant and is absorbed mainly in underground parts. The strong accumulation of Fe in macrophytes has been described by Parzych et al. [44]. According to Otte and Jakub [45], deviations from natural contents may indicate plants that may be suitable for biological monitoring. The average contents of analyzed metals in the plant material can be lined up in the following sequences: roots Fe > Mn > Zn > Cu > Co > Ni > Pb > Cr > Cd, stem Fe > Mn > Zn > Cu > Co > Ni > Pb > Cr > Cd, leaves Fe > Mn > Zn > Cu > Co > Ni > Cr > Pb > Cd.

Table 1
Basic statistical data (*n*–11) of the content of studied indicators in bottom sediments and *Phragmites australis* (root, stem, and leaf) in Biebrza river

Element mg kg^{-1} DM	Ni	Co	Pb	Cu	Zn	Fe	Mn	Cr	Cd
					Root				
Min-max	2.6–8.8	4.5–13.3	1.1–11.5	12.6–20.7	32.3–68.5	2,096–1,4786	79–603	1.6–9.6	0.13–0.61
Mean ± SD	5.3 ± 2.1	8.7 ± 2.7	5.1 ± 3.3	16.7 ± 2.6	50.5 ± 12.2	9,153 ± 4,651	408 ± 204	4.5 ± 2.6	0.42 ± 0.15
Coefficient of variation (%)	38.5	31.5	64.7	15.5	24.2	50.8	50.2	56.5	36.7
S-W test	0.2	0.98	0.17	0.52	0.63	0.04	0.03	0.09	0.45
					Stem				
Min-max	1.2–3.7	1.1–6.4	0.2–2.0	8.5–17.2	1.3–50.1	40–1,845	35–575	0.21–3.16	0.05–0.75
Mean ± SD	2.1 ± 0.7	3.0 ± 1.5	0.9 ± 0.5	11.5 ± 2.7	33.0 ± 13.9	399 ± 521	234 ± 178	1.45 ± 0.99	0.39 ± 0.24
Coefficient of variation (%)	33.7	47.8	52.7	23.2	42.3	130.6	76.2	67.91	62.43
S-W test	0.20	0.21	0.16	0.18	0.27	0.00	0.34	0.26	0.64
					Leaf				
Min-max	1.5–4.3	0.9–7.9	0.2–2.3	9.3–14.3	16.9–34.4	61–3,910	42–527	0.1–3.3	0.02–0.51
Mean ± SD	2.3 ± 0.8	3.3 ± 1.9	1.2 ± 0.7	11.6 ± 1.7	24.7 ± 4.6	711 ± 1,119	241 ± 190	1.3 ± 1.2	0.32 ± 0.16
Coefficient of variation (%)	35.7	57.1	55.5	15.2	18.6	157.3	78.9	93.2	50.0
S-W test	0.08	0.07	0.76	0.18	0.45	0.00	0.09	0.04	0.16
					Bottom sediments				
Min-max	1.3–6.6	1.9–9.5	0.39–9.3	6.8–15.2	5.2–92.8	1,093–6,476	18–363	0.4–4.7	0.01–0.53
Mean ± SD	3.6 ± 1.8	4.8 ± 2.7	4.2 ± 3.3	10.8 ± 3.2	31.0 ± 25.1	2,680 ± 1,727	98 ± 93	2.1 ± 1.6	0.20 ± 0.2
Coefficient of variation (%)	50.2	56.9	78.4	30.7	80.9	64.5	94.8	76.8	91.7
S-W test	0.18	0.15	0.25	0.10	0.06	0.05	0.00	0.05	0.09
pH min-max	7.6–8.2								
MO (%) min-max	0.2–1.3								
Natural levels in plants	0.1–5[a]	0.01–0.8[a]	0.1–5[b]	5–30[a]	10–70[b]	50–200[b]	20–500[a]	0.02–0.5[a]	0.05–0.2[a]
Geochemical background	68[c] 5[d]	19[c] 2[d]	20[c] 10[d]	45[c] 6[d]	95[c] 48[d]	47,700[c]	850[c]	90[c] 5[d]	0.3[c] 0.5[d]

[a]Kabata-Pendias and Pendias [27], [b]Markert [28], [c]Turekian and Wedephol [29], [d]Bojakowska [24].

Table 2
Value of the geochemical index (I_{geo}) in bottom sediments of Biebrza river

Metal	Ni	Co	Pb	Cu	Zn	Fe	Mn	Cr	Cd
I_{geo}	–4.62 ± 0.64	–2.40 ± 0.61	–2.75 ± 1.06	–2.41 ± 0.65	–2.20 ± 1.32	–4.38 ± 0.70	–3.38 ± 0.95	–5.72 ± 0.82	–0,34 ± 0.74

3.3. Bioconcentration factor and translocation factor coefficients

To assess the movement of metals from sediment to the roots of plants, the bioconcentration factor (BF) was calculated as shown in Table 3.

The average value of BF was increased in the following order: Mn > Fe > Cr > Cd > Co > Zn > Ni > Cu > Pb. The tests have shown higher metal contents in the roots of *Phragmites australis* than in sediments and the BF coefficient exceeded the unity. *Phragmites australis* can be used to phyto-stabilize contaminated bottom sediments, because metals are taken up by the roots, limiting mobility to above-ground parts [46]. Therefore, *Phragmites australis* can be considered the root battery of these metals [47].

The translocation factor (TF) provides information on the internal transport of metals within the plant. Values of translocation coefficients illustrate the mobility of analyzed metals in the stem-root and leaf-root relationship. TF > 1 values indicate a high degree of movement. The obtained mean values of the transport coefficient from roots to stems

Table 3
Transfer factor of metals from roots to other organs of *Phragmites australis* from Biebrza river (mean)

Element	Root/sediment	Stem/root	Leaf/root
Ni	1.50	0.41	0.44
Co	1.82	0.35	0.37
Pb	1.21	0.17	0.23
Cu	1.44	0.69	0.71
Zn	1.62	0.65	0.49
Fe	3.42	0.10	0.11
Mn	4.11	0.57	0.59
Cr	2.17	0.32	0.28
Cd	2.11	0.92	0.76

and leaves are smaller than 1.0 (Table 3). Mobility of tested metals in *Phragmites australis* differed in the analyzed parts (stem, leaf). Higher TFs were recorded for most of the studied elements between roots and leaves with the exception of Zn, Cr, and Cd, for which TF was higher between the root and the stem. The lowest TF values were recorded for Fe (stem/root - 0.10 and leaf/root - 0.12), which, combined with high BCF - 3.42, suggests that *Phragmites australis* can be used to phyto-stabilize the Fe-contaminated sediments.

4. Interpretation of results using statistical analyses

Statistical analyses began with the Shapiro-Wilk normality test. The test results indicate that most variables have a normal distribution. The variability of the parameters examined was tested on the basis of the coefficient of variability. High values of the variability coefficient indicate the presence of sources of the metals tested, while the small ones may indicate their contents close to natural ones. During the analyses, it was noticed that variables characterized by large values of variability coefficients did not have normal distribution as opposed to variables with small coefficients of variation, which had a normal distribution.

During the analyses, in the majority of cases, higher values of coefficients of variability for a specific metal in bottom sediments were observed in comparison with individual organs of the studied plants (Table 1). It can be deduced from this that bottom sediment is more susceptible to external contaminants compared to macrophytes. Research by Jia et al. [48] showed another element of the aquatic environment, in which the variability of metals occurrence is greater than in bottom sediments. This element is water. It is known that water is more vulnerable to seasonal fluctuations, therefore bottom sediment is more appropriate to assess the level of ecological threats to the aquatic environment. According to MacDonald et al. [49], bottom sediment is a good indicator for assessing the long-term impact of metals on the aquatic environment.

The paper does not include the Pearson correlation matrix showing the relationships between investigated metals in bottom sediments and organs of aquatic plants as well as MO and pH due to its size. However, attention was paid to the most characteristic dependencies from the points of view of the issues described in the publication. Strong Pearson correlations were observed from $r = 0.60$ to $r = 0.90$ between metals in bottom sediments, which may indicate their common sources. But this mechanism is not always present, which was confirmed by research conducted by Ma et al. [50]. Analyses also indicate positive relationships between the amount of MO and metals in sediments, as shown by Pearson correlation coefficients ranging from $r = 0.69$ to $r = 0.92$. MO binds metal ions immobilizing them in bottom sediments. Iron present in the sediments also binds to ions of the investigated metals, which is indicated by large values of Pearson correlation coefficients $r = 0.61$ to $r = 0.90$. The well-known metal adsorption mechanism on iron oxides has been of key importance here. The behavior of metals in bottom sediments is also strongly influenced by the reaction of sediments. Analyses revealed negative significant Pearson correlation coefficients from $r = –0.44$ to $r = –0.88$ between the reaction of sediments and the content of metals in them. Metals present in more acidic sediments may change their form to a more mobile. Sediment reaction is one of the most important of their properties affecting the behavior of metals and other components.

In order to identify possible sources of heavy metals in sediments and macrophytes, a multivariate statistical analysis (FA) was used. FA is widely used to identify sources of pollution [51–54]. On the basis of FA, a large number of variables was reduced to only two (factor 1 and factor 2) based on the "scree criterion" and "Kaiser criterion" together representing 52% of global variability of phenomena and processes occurring in the analyzed system (Table 4).

Factors 1 and 2 are correlated with some variables based on significant so-called factor loads, the values of which are greater than 0.7. The obtained factor loads are equivalents of correlation coefficients. Factor loads can also correlate with each other. Factor 1, explaining 33% variability, is correlated with metals present in sediments and may indicate active point and surface sources of these elements within the Biebrza river. A positive factor load representing MO is also associated with its supply to sediments from river catchment regions. The catchment area is forests, wetlands and peat bogs. MO has binding properties in relation to metals as previously indicated. The enrichment mechanism is the main mechanism in the analyzed system as indicated by the level of the total variance (variability) - 33%. The second factor 2, which explains only 19% of variability, is associated with enrichment in metals in most cases of leaves of the studied macrophytes. Places, from which samples of sediments and aquatic plants (macrophytes) were collected, were usually located near bridges, through which communication routes run. Moving car vehicles are the source of the so-called road dust generated mainly during braking, abrasion of tires on the road surface, abrasion of brake pads and corrosion. As indicated by domestic and foreign studies, road dust contains large amounts of metals that can accumulate and migrate within the environment [55,56]. Therefore, metals contained in macrophyte leaves can pass from road dust accumulating on their surfaces during the movement of vehicles car. Therefore, factor 2 allowed for the identification of the second source of metals within the Biebrza river, that is, moving motor vehicles on roads running on bridges. However, factor 1 has the most impact on the supply of metals to the Biebrza river. To carry out

Table 4
Factor analysis results (FA), factor loads >0.70

Variables		Factor 1	Factor 2
Ni	Sediment	0.97	0.21
	Root	0.18	–0.04
	Stem	0.16	0.63
	Leaf	0.54	0.81
Co	Sediment	0.95	–0.07
	Root	0.09	–0.05
	Stem	0.22	0.61
	Leaf	0.32	0.87
Pb	Sediment	0.88	0.03
	Root	–0.00	–0.10
	Stem	0.61	0.47
	Leaf	–0.03	0.74
Cu	Sediment	0.83	0.13
	Root	0.23	0.40
	Stem	–0.34	0.78
	Leaf	0.50	0.48
Zn	Sediment	0.88	–0.08
	Root	0.38	0.05
	Stem	–0.11	0.34
	Leaf	0.10	0.48
Fe	Sediment	0.79	0.22
	Root	–0.71	0.13
	Stem	–0.38	–0.13
	Leaf	0.03	0.36
Mn	Sediment	0.44	0.22
	Root	–0.75	0.20
	Stem	–0.70	–0.26
	Leaf	–0.79	0.28
Cr	Sediment	0.89	0.22
	Root	–0.29	0.16
	Stem	–0.13	0.72
	Leaf	0.29	0.67
Cd	Sediment	–0.66	–0.25
	Root	0.59	–0.66
	Stem	0.19	–0.77
	Leaf	–0.01	–0.88
M		0.88	0.40
Sediment pH		–0.75	–0.15
Explained variance		33%	19%

further analysis of the reduced amount of data, the values of unobservable variables (factors 1 and 2) should be estimated. Estimations obtained (quantities determined based on a sample to assess the entire population) are called factor values. Distribution of factor values was analyzed along the river surveyed in Fig. 2.

The largest factor values representing factor 1 were at the source point of the Biebrza River and at the point named Polkowo. Before the research point - the source has its estuary in the tributary of the Biebrza River – Sidra River. The largest sources of contamination of the Sidra River include the Agricultural School in Różany Stok and mechanical and biological treatment plant processing 65 m^3 of sewage daily. Sidra is a small river with irregular banks flowing through farmland, meadows, and pastures where cattle graze. In addition, the Sidra River is supplied with drainage ditches along its entire length. Agricultural activity related to fertilization, mechanization of agriculture and field runoff is, in this case, the main source of metals at this point. Before the Polkowo point, the Augustów Canal flows into the Biebrza River, collecting pollution from the urbanized area of Augustów, sewage treatment plants, and surrounding fields and pastures. This is the main source of metals at this point. Factor 2 is related to the absorption of metals through the leaves of macrophytes. The origin of metals absorbed by macrophytes is associated with road dust generated on communication bridges. The biggest impact of the second factor takes place in the following points: Ostrów, Polkowo, Osowiec, and Rutkowskie.

Zhang et al. [57] used HCA to characterize spatial changes in surface water quality and to classify a possible source based on a relatively small, short-term data set. The HCA cluster analysis was carried out to assess the similarity of groups that create sampling sites. The applied statistical method HCA (Fig. 3) allowed to divide 11 sampling points into two groups (clusters).

The first cluster 1 (Jagłowo, Rutkowskie, Osowiec, Brzostowo, Goniądz, Sztabin, and Ostrowie) was identified, as well as cluster group 2 (Dolistowo, Lipsk, Polkowo, springs of Biebrza river). It turned out that before the points included in the first group (cluster 1), there are no tributaries of the Biebrza river in the form of rivers, canals or streams. However, before the points forming the second group (cluster 2), such tributaries occur Dolistowo - a tributary of Brzozówka river, Lipsk and the springs of Biebrza river - Sidra river and Polkowo - the Augustów Canal. In addition, in Augustów, ($Q_{dśr}$ –3850 $m^3\ d^{-1}$), Lipsk ($Q_{dśr}$ –250 $m^3\ d^{-1}$) and Dolistowo ($Q_{dśr}$ –120 $m^3\ d^{-1}$), the largest municipal sewage treatment plants in Biebrza river catchment are located. In connection with the above, the CA analysis allowed us to identify the point sources of Biebrza river pollution in the form of its tributaries and sewage treatment plants transporting contaminants from agricultural and urban areas.

5. Summary

Analysis of results of the geo-accumulation index for all analyzed trace elements showed that bottom sediments collected from the Biebrza River are uncontaminated (class 0). The research of plant material showed that the highest contents of studied elements occur in the roots of *Phragmites australis*. Limited mobility and translocation of metals present in the plant make it a good species for the phytostabilization of bottom sediments, in particular in the case of Fe. Analysis of Pearson correlation revealed a common source of metals detected in the bottom sediments of the Biebrza River. Metals are bound to a large extent by MO and iron oxides. FA allowed identifying two sources of metals in sediments and macrophytes. The first source, as more important, are active point and surface sites associated with municipal and agricultural management. The second

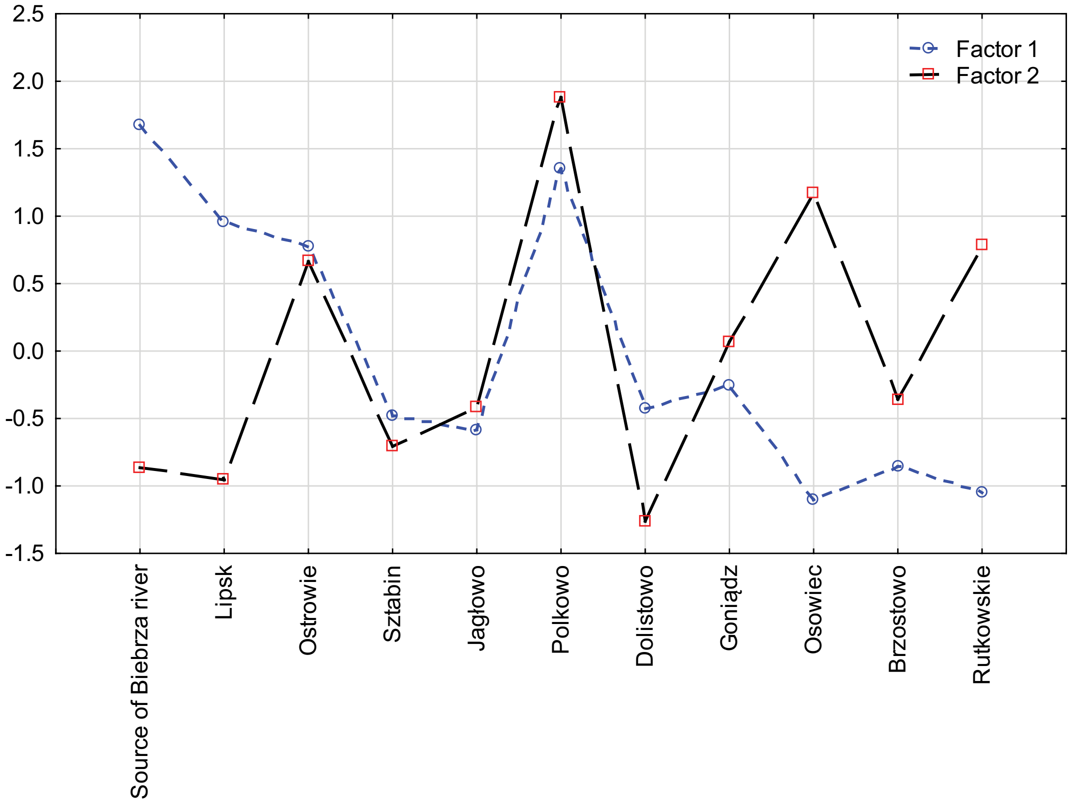

Fig. 2. Linear variability of factor values (FA) along the Biebrza river.

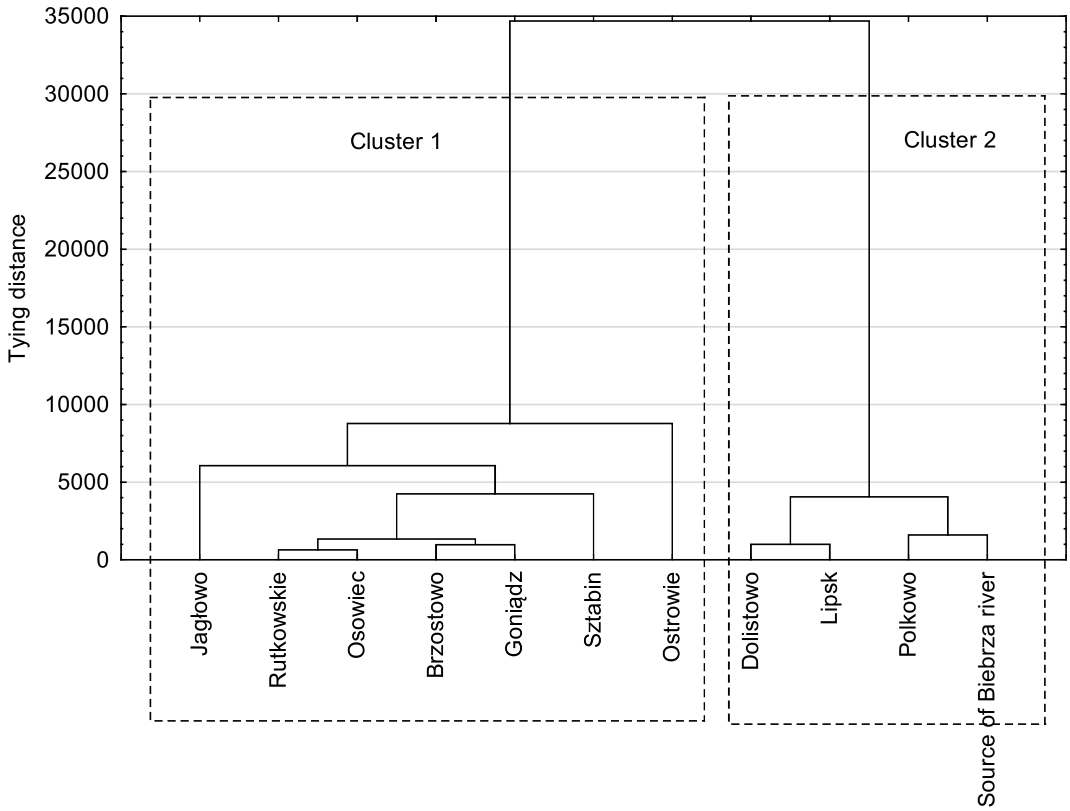

Fig. 3. Dendrogram based on hierarchical grouping (HCA - Ward).

source, no longer relevant, is associated with road dust produced by moving motor vehicles on roads located on the bridges of Biebrza River.

Statistical models (FA and HCA) allowed to identify the main routes of metals transport from Biebrza river catchment. These are canals, streams and ditches draining the area diversified in terms of use.

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References

[1] D.M. Cooper, W.A. House, B. Reynolds, S. Hughes, L. May, B. Gannon, The phosphorus budget of the Thame catchment, Oxfordshire: 2. Modelling, Sci. Total Environ., 282–283 (2002) 435–457.

[2] C.A. Harguinteguy, A.F. Cirelli, L.M. Pignata, Heavy metal accumulation in leaves of aquatic plant *Stuckenia filiformis* and its relationship with sediment and water in the Suquía river (Argentina), Microchem. *J.*, 114 (2014) 111–118.

[3] M. Klavins, A. Briede, V. Rodinov, I. Kokorite, E. Parele, I. Klavina, Heavy metals in rivers of Latvia, Sci. Total Environ., 262 (2000) 175–183.

[4] I. Ali, C.K. Jain, Pollution potential of toxic metals in the Yamuna river at Delhi, India, J. Environ. Hydrol., 12 (2001) 1–9.

[5] A. Samecka-Cymerman, A.J. Kempers, Toxic metals in aquatic plants surviving in surface water polluted by copper mining industry, Ecotoxicol. Environ. Saf., 59 (2003) 64–69.

[6] D. Demirezen, A. Aksoy, Accumulation of heavy metals in *Typha angustifolia* (L.) and *Potamogeton pectinatus* (L.) living in Sultan Marsh (Kayseri, Turkey), Chemosphere, 56 (2004) 685–696.

[7] A.T. Hejabi, H.T. Basavarajappa, Heavy metals partitioning in sediments of the Kabini River in South India, Environ. Monit. Assess., 185 (2013) 1273–1283.

[8] L. Polechońska, A. Klink, Trace metal bioindication and phytoremediation potentialities of *Phalaris arundinacea* L. (reed canary grass), J. Geochem. Explor., 146 (2014) 27–33.

[9] M.V. Kumar, B.D. Tripathi, Concurrent removal and accumulation of heavy metals by the three aquatic macrophytes, *Bioresour.* Technol., 99 (2008) 7091–7097.

[10] D.M. Dong, H.L. Li, Y. Li, C.S. Fang, X.H. Li, C.Y. Xu, Distribution of heavy metals in the sediments from the Yitong River: Changchun Section, J. Soil Water Conserv., 11 (2004) 95–96.

[11] L. Marchand, F. Nsanganwimana, B.J. Cook, Y. Vystavna, F. Huneau, P. Le Coustumer, J.B. Lamy, N. Oustrière, M. Mench, Trace element transfer from soil to leaves of macrophytes along the Jalled'Eysines River, France and their potential use as contamination biomonitors, Ecol. Indic., 46 (2014) 425–437.

[12] I. Panfili, M.L. Bartucca, D. Del Buona, The treatment of duckweed with a plant biostimulant or a safener improves the plant capacity to clean water polluted by terbuthylazine, Sci. Total Environ.,1 (2019) 832–840.

[13] E. Skorbiłowicz, Studies upon Some Metals Distribution over the Aqueous Environment in Upper Narew River Catchment, Scientific Work nr 222, Białystok, Publishing House of the Białystok University of Technology, 2012. (In polish)

[14] A.J. Cardwell, D.W. Hawker, M. Greenway M. Metal accumulation in aquatic macrophytes from southeast Queensland, Australia, Chemosphere, 48 (2002) 653–663.

[15] M. Fawzy, M. Badr, A. El-Khatib, A. Abo-El-Kassem, Heavy metal biomonitoring and phytoremediation potentialities of aquatic macrophytes in River Nile, Environ. Monit. Assess., 184 (2012) 1753–1771.

[16] T. Sawidis, M.K. Chettri, G.A. Zachariadis, J.A. Stratis, Heavy metals in aquatic plants and sediments from water systems in Macedonia, Greece, Ecotoxicol. Environ. Saf., 32 (1995) 73–80.

[17] A. Sasmaz, E. Obekb, H. Hasar, The accumulation of heavy metals in *Typha latifolia* L. grown in a stream carrying secondary effluent, Ecol. Eng., 33 (2008) 278–284.

[18] G. Bonanno, Trace element accumulation and distribution in the organs of *Phragmites australis* (common reed) and biomonitoring applications, Ecotoxicol. Environ. Saf., 74 (1995) 1057–1064.

[19] G. Du Laing, F.M.G. Tack, M.G. Verloo, Performance of selected destruction methods for the determination of heavy metals in reed plants (*Phragmites australis*), Anal. Chim. Acta., 497 (2003) 191–198.

[20] E. Skorbiłowicz, Macrophytes as indicators of heavy metals bio-accumulation in upper Narew River, Ecol. Chem. Eng. A, 21 (2014) 87–98.

[21] Z.W. Kundzewicz, Ecohydrology for Sustainable Wetlands under Global Change – Data, Models, Management, S. Ignar, P. Nowakowski, T. Okruszko, Eds., Wethydro – Center of Excellence in Wethland Hydrology, SGGW Publisher, Warszawa, 2003, pp. 25–35. (In Polish)

[22] M. Anaszko, S. Grocki, Protection of Resources and Values of the Natural Environment of the Biebrza Marshland, Studia-regionalne, 2(4), University of Economics Publisher, Białystok, 2001, pp. 9–54. (In Polish)

[23] A. Górniak, The Climate and Thermics of the Surfacewaters of the Biebrza Basin, Economy and Environment Publishing House, Białystok, 2004, pp. 345–362. (In Polish)

[24] I. Bojakowska, Criteria for assessing the pollution of water sediment, Geol. Rev., 49 (2001) 213–218. (In Polish)

[25] J. Lis, A. Pasieczna, Geochemical Atlas of Poland 1:2 500 000, Polish Geological Institute, Warszawa, 1995. (In Polish)

[26] Z. Mazej, M. Germ, Trace element accumulation and distribution in four aquatic macrophytes, Chemosphere, 74 (2009) 642–647.

[27] A. Kabata-Pendias, H. Pendias, Trace Elements in Soils and Plants, 3rd ed., CRC Press, Boca Raton, London, New York, Washington, D.C., 2001.

[28] B. Markert, Presence and significance of naturally occurring chemical elements of the periodic system in the plant organism and consequences for future investigations on inorganic environmental chemistry in ecosystems, Vegetatio, 103 (1992) 1–30.

[29] K.K. Turekian, K.H. Wedepohl, Distribution of the Elements in some major units of the Earth's crust, GSA, Bulletin, 72 (1961) 175–192.

[30] G. Müller, Schwermetalle in den sedimenten des Rheins, Veranderungen Seit 1971 Umschau, 79 (1979) 778–783.

[31] C.S. Lee, X.D. Li, W.Z. Shi, S.C. Cheung, I. Thornton, Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics, Sci. Total Environ., 356 (2006) 45–61.

[32] D.W. Alberto, D.M. Del Pilar, A.M. Valerial, P.S. Fabianal, H.A. Cecilia, B.M. De Los Angeles, Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquia river basin (Cordoba-Argentina), Water Res., 35 (2001) 2881–2894.

[33] A. Astel, S. Tsakovski, P. Barbieri, V. Simeonov, Comparison of self-organizing maps classification approach with cluster and principal components analysis for large environmental data sets, Water Res., 41 (2007) 4566–4578.

[34] T.G. Kazi, M.B. Arain, M.K. Jamali, N. Jalbani, H.I. Afridi, R.A. Sarfraz, J.A. Baig, A.Q. Shah, Assessment of water quality of polluted lake using multivariate statistical techniques: a case study, Ecotoxicol. Environ. Saf., 72 (2009) 301–309.

[35] S. Shrestha, F. Kazama, Assessment of surface water quality using a multivariate statistical techniques: a case study of the Fuji river basin, Japan Environ. Modell. Software, 22 (2007) 464–475.

[36] L.G. Vardanyan, B.S. Ingole, Studies on heavy metal accumulation in aquatic macrophytes from Sevan (Armenia) and Carambolim (India) lake systems, Environ. Int., 32 (2006) 208–218.

[37] D. Baldantoni, A. Alfani, P. Di Tommasi, G. Bartoli, A.V. De Santo, Assessment of macro and microelement accumulation capability of two aquatic plants, Environ. Pollut., 130 (2004) 149–156.
[38] H. Vereecken, J. Baetens, P. Viaene, F. Mostaert, P. Meire, Ecological management of aquatic plants: effects in lowland streams, Hydrobiologia, 570 (2006) 205–210.
[39] J. Srivastava, A. Gupta, H. Chandra, Managing water quality with aquatic macrophytes, Rev. Environ. Sci. Biotechnol., 7 (2008) 255–266.
[40] A. Aksoy, D. Demirezen, F. Duman, Bioaccumulation, detection and analyses of heavy metal pollution in Sultan marsh and its environment, Water Air Soil Pollut., 164 (2005) 241–255.
[41] A. Parzycha, M. Cymer, The content of macro- and microelements in the shoots of Glyceria Maxima of the Słupia river, J. Ecol. Eng., 15 (2014) 29–36.
[42] E.I. Hozhina, A.A Khramov, P.A. Gerasimov, A.A. Kumarov, Uptake of heavy metals, arsenic and antymony by aquatic plants in the vicinity of ore mining and processing industries, J. Geochem. Explor., 74 (2001) 153–162.
[43] S.E. Allen, Analysis of Ecological Materials, 2nd ed., Blackwell Scientific Publications, Oxford, 1986.
[44] A. Parzych, M. Cymer, J. Jonczak, S. Szymczyk, The ability of leaves and rhizomes of aquatic plants to accumulate macro- and micronutrients, J. Ecol. Eng., 16 (2015a) 198–205.
[45] M.L. Otte, D.L. Jacob, Chemical fingerprinting of plants from contrasting wetlands - salt marsh, geothermal and mining impacted, Phyton, 45 (2005) 303–316.
[46] E.M. Eid, K.H. Shaltout, M.A. El-Sheikh, T. Asaeda, Seasonal courses of nutrients and heavy metals in water, sediment and above- and below-ground *Typha domingensis* biomass in Lake Burullus (Egypt): perspectives for phytoremediation, Flora, 207 (2012) 783–794.
[47] M.M. Abreu, E.S. Santos, M.C.F. Magalhães, E. Fernandes, Trace elements tolerance, accumulation and translocation in *Cistus populifolius*, *Cistus salviifolius* and their hybrid growing in polymetallic contaminated mine areas, J. Geochem. Explor., 123 (2012) 52–60.
[48] Y. Jia, L. Wang, Z. Qu, Z. Yang, Distribution, contamination and accumulation of heavy metals in water, sediments, and freshwater shellfish from Liuyang River, Southern China, Environ. Sci. Pollut. Res., 25 (2018) 7012–7020.
[49] D.D. MacDonald, C.G. Ingersoll, T.A. Berger, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems, Arch. Environ. Contam. Toxicol., 39 (2000) 20–31.
[50] L. Ma, Z. Yang, L. Li, L. Wang, Source identification and risk assessment of heavy metal contaminations in urban soils of Changsha, a mine-impacted city in Southern China, Environ. Sci. Pollut. Res., 23 (2016) 17058–17066.
[51] T. Kowalkowski, R. Zbytniewski, J. Szpejna, B. Buszewski, Application of chemometrics in river water classification, Water Res., 40 (2006) 744–752.
[52] Y. Ouyang, P. Nkedi-Kizzab, Q.T. Wu, D. Shinde, C.H. Huang, Assessment of seasonal variations in surface water quality, Water Res., 40 (2006) 3800–3810.
[53] S. Shrestha, F. Kazama, Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan Environ. Modell. Software, 22 (2007) 464–475.
[54] F. Zhou, G.H. Huang, H. Guo, W. Zhang, Z. Hao, Spatio-temporal patterns and source apportionment of coastal water pollution in eastern Hong Kong, Water Res., 41 (2007) 3429–3439.
[55] E. Adamiec, Traffic-related metals as sources of urban environment pollution: a case study of Kraków, Poland, WIT Trans. Ecol. Environ., 214 (2017) 81–89.
[56] E.M.E. Alsbou, O.A. Al-Khashman, Heavy metal concentrations in roadside soil and street dust from Petra region, Jordan, Environ. Monit. Assess., 190 (2017) 48.
[57] Q. Zhang, Z.W. Li, G.M. Zeng, J.B. Li, Y. Fang, Q.S. Yuan, Y.M. Wang, F.Y. Ye, Assessment of surface water quality using multivariate statistical techniques in red soil hilly region: a case study of Xiangjiang watershed, China, Environ. Monit. Assess., 152 (2009) 123–131.