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Assessment of Minor and Trace Elements in Aquatic Macrophytes, Soils and Bottom Sediments Collected along Different Water Objects in the Black Sea Coastal Zone by Using Neutron Activation Analysis

Pavel Nekhoroshkov[1], Alexandra Kravtsova[1], Alexander Kamnev[2], Olga Bun'kova[3], Octavian Duliu[4], Marina Frontasyeva[1], Igor Yermakov[2]

[1]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia
[2]Faculty of Biology, Lomonosov Moscow State University, Moscow, Russia
[3]Faculty of Soil Science, Lomonosov Moscow State University, Moscow, Russia
[4]Department of the Structure of Matter, Earth and Atmospheric Physics, and Astrophysics, Faculty of Physics, University of Bucharest, Bucharest, Romania
Email: nekhoroshkov@gmail.com

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Abstract

The levels and compartmentalization of Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, Au, Th, and U in *Phragmites australis* (Cav.) Trin. ex Steud., *Carex conescens* L. and *Cladophora sericea* (Hudson) Kutzing from the Caucasian coast of the Black Sea-Anapa recreational region was investigated by Neutron Activation Analysis. The study touches upon subject of the sediment-to-plant and root-to-leaf elemental transfer as well as of the influence of anthropogenic pollution on wetland ecosystems in zone of resort. The content of the majority of considered elements was found higher in the belowground organs of *P. australis* than in the aboveground tissues while a reverse regularity was evidenced for *C. conescens*. The levels of elements decrease from bottom sediments to aquatic plants with the notable exception of the halogens Cl, Br and I that presented 5 to 100 fold higher content in plants than in sediments. The increased levels of As, Mo, and Sb in some soil and sediment samples most probably indicate the anthropogenic pollution. It recommends them for a continuous monitoring of the same area.

Keywords

Trace Elements, Neutron Activation Analysis, The Black Sea, *Phragmites*

Australis (Cav.) Trin. ex Steud., *Carex conescens* L., *Cladophora sericea* (Hudson) Kutzing

1. Introduction

The aquatic macrophytes are widely used for assessing the environmental situation in fresh as well as seawater [1]-[10]. As the accumulation of trace metals in organisms depends on the concentration of pollutants in water and sediments as well as on exposure time, a tissue analysis of aquatic macrophytes may provide cumulative evaluation of exposure [1] [6] [11] [12] [13].

The concentrations of chemical elements in aquatic plants can be more than 100,000 times higher than in the associated water [1] [14]. This accumulation ability of certain macrophytes is used for monitoring purposes in relatively clean and recreation zones where low level of contamination might be difficult to detect [15].

Our previous investigations in polluted waters of the Black Sea region [16] [17] [18] evidenced the increased elemental concentrations in marine algae reflecting their great potential for biomonitoring water quality. They proved not only the existence of a certain degree of anthropogenic contamination but also the suitability of aquatic plants for biomonitoring trace elements.

To extend our studies regarding the elemental content of more than 35 elements for the territory of an important but poor investigated recreation zone of the Caucasian coast of the Black Sea, the aquatic macrophytes *Phragmites australis*, *Carex conescens* L. as well as the green algae *Cladophora sericea* (Hudson) Kutzing. were used.

P. australis is one of the most distributed macrophytes in aquatic ecosystems, and numerous studies showed its capacity of trace element bioaccumulation [11] [13] [15] [19] [20] [21] [23]. Thus Duman [19] reported that the roots of *Phragmites australis* from fresh water Lake Sapanca in Turkey were found to be good accumulators of Cu, Mn, Ni, Zn. The studies of [15] [22] in the estuaries of Italian rivers affected by municipal wastewaters and agricultural activities showed a good correlation of Al, As, Cr, Cu, Mn, Ni and Zn in P. australis with the elemental content in corresponding sediments and water. Also a strong positive correlation between the concentrations of Al, As, Co, Cr, Cu, Fe, Mn, Ni, Se, Sr and Zn in the sediments and all organs (rhizome, stem and leave) of P. australis sampled from the Tisza River in Serbia was found by [23]. The investigations in the constructed wetland in North Italy [24] and in the Hokersar wetland, Ramsar site of Kashmir Himalaya, India [25] showed that *P. australis* is appropriate species for phytoextraction and phytoremediation of the environment. Analysis of the elemental composition of *P. australis*, collected in the Anapa region in 2013-2014, showed that the concentration ratios with the absolute value that is greater than 1 (pointing to the pollution of the area) are determined only for As. Maximal values of biological absorption coefficients were found for the

As, Fe, K, Mn, Zn in roots [13].

The data of using the species of *Carex* (sedges) in biomonitoring purposes are scarce in comparison with *Phragmites*. Horovitz [26] reported the content of Ag, Co, Cr, Cs, Fe, Rb, Sc, Th, Zn and in *Carex pendula* sampled in botanical garden in Germany. Pederson and Harper [27] studied the chemical composition of some major forage plants of mountain summer ranges of southeastern Utah, USA, reported the content of K, Ca and Mg in *Carex geyeri*. Ohlson [28] studied the content of Al, Ca, Cu, Fe, K, Na, Mg, Mn, Mo, Zn in eleven plants from the mires of central and north Sweden, and he found that the largest variation in elemental concentration of roots and leaves was observed in *Carex rostra*. He also reported that the concentration of K in tissues of *Carex* species was highly correlated with its concentration in the substrate.

The species of green algae of genus *Cladophora* has frequently been suggested as a suitable organism to monitor water contamination and its practical use in monitoring river, lake and sea pollution has been reported from a range of countries [29]-[34]. Thus Whitton *et al.* [29] reported that there were highly significant correlations between Cu, Fe, Zn content in *Cladophora glomerata* from rivers and streams in Northern England and water. The similar results were reported by [31] for Cr, Ni and V determined in *Cladophora glomerata* from refinery sewage lagoon (Bratislava). Levkov and Krstic [33] found that the levels of Co, Cu, Fe, Mn and Zn in *Cladophora glomerata* reflected their load in the River Vardar, Macedonia, and recommended it as a precise biomonitoring tool for determination and quantification of heavy metal pollution in this river. In [34] the distribution patterns of Ca, Cu, K, Mg, Mn, Na, Ni, Zn and in the green algae *Cladophora* sp. from the Southern Baltic is assessed. The study concluded that *Cladophora* sp. can be used the most successfully as biomonitor of Cu and Zn content in the Baltic Sea because of its ability to accumulate metal contaminants from seawater, tolerance to metals, simple morphology and adequate tissue for analysis.

The preliminary study [13] of elemental composition of *Cladophora sericea*, collected in the Anapa region in 2013, showed that the plant to soil ratios greater than one and pointing towards a possible contamination process were detected only for As, and Sr.

For our study, we have chosen three types of phototrophic macrophytes as ones of the most convenient organisms-biomonitors. Moreover, they occur in different ecological conditions and are the first ones that take the fall of the coastal pollution runoff [11] [13]. Accordingly, we have investigated the hydrophyte filamentous marine green alga *Cladophora sericea* (Hudson) Kutzing, helophyte *Phragmites australis* (Cav.) Trin. Ex Steud as well as the hygrophyte *Carex conescens* L.

Cladophora sericea lives in shallow sandy areas of the Black Sea; absorbs minor and trace elements by all surface of its body, dosen’t have root system [31], *Phragmites australis* lives along the coastal zones of rivers and seas. The well-developed root system makes more than 80% of the total biomass. Plants absorb minor and trace elements from soil, sediment and water by additional roots [15] [20]. *Carex conescens* L. grows on the banks of the rivers. Unlike *Phragmites australis*, it is a plant which has a small root system, so it absorbs minor and trace elements only from the soil [26].

The main goals of the study consist of: 1) quantifying the content of a wide range of major as well as trace elements in *Phragmites australis*, *Carex conescens*, *Cladophora sericea* and corresponding soil and bottom sediments samples; 2) assessing the elemental content in different parts of plants (leaves, roots); 3) quantifying the element mobility from sediment to organs, as well as within the plant; 4) providing new data on the geochemistry of sediments and soil from the Anapa region; 5) quantifying the level of the anthropogenic pollution of the study area. The results of this project will be further presented and discussed.

2. Materials and methods

2.1. Study Area and Sampling

A resort city of Anapa (Krasnodar region) located on the Caucasian coast of the Black Sea is characterized by humid subtropical climate and long sandy beach. The Anapka river crossing the territory of the town connects Anapa reed beds with the Black Sea [35].

The investigated area (**Figure 1**, **Table 1**) includes the municipal waste dump at the Krasnyi hutor and some reservoirs, *i.e.* a lake, a river and reed beds at the foot of the hill and below the dump situated on the highland. These water bodies form an indivisible watershed of the river Anapka which estuary occupies the main city beach within the city recreation zone. The solid waste city dump of Anapa (**Figure 1**, st. 6) is located near the Krasnyi hutor, 4.65 km from the Black Sea. During 10 years, the total area of the dump increased from 9 to 26 hectares in 2013 [35]. There is a lake located in the distance of 1 km downhill from the dump at village Krasnyi hutor (**Figure 1**. st. 7). The next sampling point is Anapa reed beds (**Figure 1**, st. 8). This marshland is situated at the hollow, where the Kotloma and Kumatyr Rivers get its confluence, not far from the Anapa station. The length of the Anapka reed beds (**Figure 1**, st. 2a) is 1.7 km long. The station 2b is situated in old bed of the Anapka river. The mouth of the Anapka river (**Figure 1**, st. 2c) is located at the main city beach (**Figure 1**, st. 2d).

The samples of vegetation (live and dead leaves and roots of *Phragmites* and *Carex*, algae *Cladophora*) (n = 35) and the corresponding soil (n = 40) and bottom sediment (BS) (n = 15) were collected at 7 sites along the transect located near Anapa city in summer of 2013 and 2014. The sampling sites are shown in **Figure 1** while **Table 1** presents more details regarding the sampling points location as well as a summary description of each category of samples. The sampling of soils, bottom sediments and plants were carried out by using standards manuals [36] [37] for studied region.

2.2. Neutron Activation Analysis

Elemental analysis of the samples was carried out by INAA at the reactor IBR-2

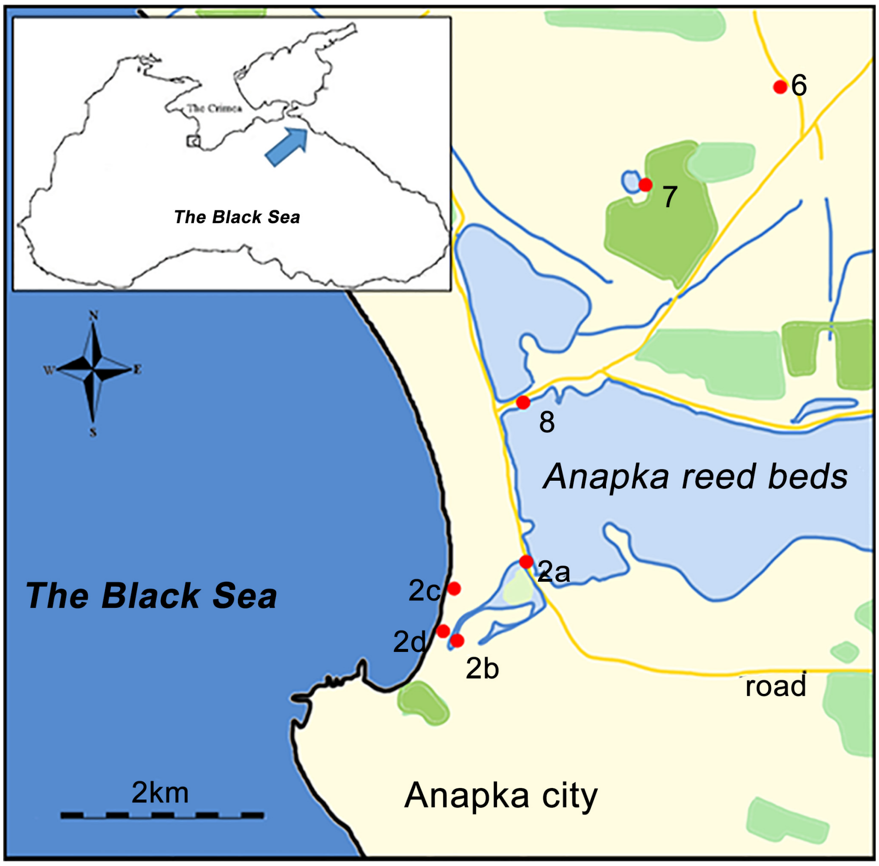

Figure 1. Sampling sites in the studied area near Anapa city (Anapa transect or cross-section).

Table 1. The location of sampling points as well as the type of collected material.

Sampling point	Latitude (N)	Longitude (E)	Type	Summary description
6. City dump	44˚57'31.76"	37˚21'51.01"	Soil	Dump without vegetation
7. Lake near Krasnyi Hutor (village)	44˚56'51.52"	37˚20'41.70"	Soil Sediments Plants	Waste liquid disposal, polluted runoff
8. Anapa reed beds	44˚55'35.97"	37˚19'47.57"	Soil Sediments Plants	Traffic, Gas station
2a. Anapka river	44˚54'35.84"	37˚19'45.33"	Soil Sediments Plants	Traffic
2b. Old bed of Anapka river	44˚54'10.27"	37˚19'10.18"	Soil Sediments Plants	Beach, objects of recreation
2c. Mouth of Anapka river	44˚54'21.59"	37˚19'06.89"	Soil Sediments Plants	Beach
2d. Anapa Bay	44˚54'11.74"	37˚19'06.87"	Sediments Plants	Beach, marine traffic

of the Frank Laboratory of Neutron Physics (FLNP) of the Joint Institute for Nuclear Research (JINR), Dubna, Russia. The analytical procedures and the basic characteristics of the employed experimental facility are described in detail elsewhere [38]. The samples of about 0.3 g were packed in polyethylene bags for short-term irradiation and in aluminum cups for long-term irradiation.

To determine the short-lived isotopes of Mg, Al, Cl, Ca, Ti, V, Mn and I the samples were irradiated for 3 min in the reactor channel with a neutron flux density of $1.3 \cdot 10^{12}$ n ($cm^{-2} \cdot s^{-1}$). Gamma spectra of induced activity were measured for 12 - 15 min after 20 min of decay. The elemental contents of the long-lived isotopes of Na, K, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Hf, Ta, Au, Th, and U were determined using epithermal neutrons in a cadmium-screened irradiation channel with a neutron flux density of $1.6 \cdot 10^{12}$ n $cm^{-2} \cdot s^{-1}$). Samples were irradiated for 90 h, repacked and then measured twice after 4 - 5 d of decay during 30 minutes and after 20 days of decay during 1.5 hours.

To process gamma spectra of induced activity and to calculate concentrations of elements in the samples, software developed at FLNP, JINR was used [39]. The uncertainties in the determined concentrations were in the range of % - 15%, and of 30% or more for those elements which concentrations in the samples were at the detection limit.

Quality control was provided by using reference materials (SRM): NIST 1632c (trace elements in coal), IAEA-433 (marine sediment), BCR-667 (estuarine sediment) as well as NIST 1515 (apple leaves) irradiated in the same conditions together with the samples under investigation. We were chosen that set of standards due to the most accurate determined values of concentrations of elements. The NAA data and certified values of reference materials are given in **Table 2**. Certified values with errors were taken from passports of SRMs, determined values with errors were calculated through neutron activation analysis in the same conditions as samples (more deep explanation is given in [38] [39]).

2.3. Data Analysis

To unify the minor and trace composition of each plant we used the Reference Plant (RP) contents [40] as normalizing factors. In this way, it was possible to compare the distribution of the considered elements in all species of plants chosen for the present study.

A similar approach we used in the case of soils and sediments by considering the Upper Continental Crust (UCC) [41] as reference average rock. Therefore, all data regarding the elemental composition of the Anapa soils and sediments samples were normalized to the corresponding content of the UCC. The accurate data on concentrations with the wide number of elements for “average sediment” are presented in UCC. The normalized on UCC data of concentrations in soils and sediments were used for comparison the levels of elements between different stations. The levels in UCC have the good agreement with the local data for Anapa region-see **Table 3**.

Table 2. The NAA data and certified values of reference materials (mean ± error, in μg·g^{-1} dry weight).

El.	SRM 1632c		SRM 433		SRM 667	
	Certified	Determined	Certified	Determined	Certified	Determined
Na	299 ± 5	300 ± 8	13500 ± 4050	13150 ± 160	-	-
Mg	384 ± 32	362 ± 15	11500 ±230	11430 ± 120	-	-
Al	9150 ± 137	9350 ± 187	78200 ± 782	77980 ± 890	-	-
Cl	1139 ± 41	1120 ± 36	-	-	-	-
K	1100 ± 33	1100 ± 201	16600 ± 2224	16300 ± 250	-	-
Ca	1450 ± 290	1430 ± 130	-	-	-	-
Sc	2.9 ± 0.03	2.91 ± 0.07	14.6 ± 4.38	15.1 ± 0.15	13.7 ± 0.7	12.3 ± 0.24
Ti	517 ± 32	511 ± 21	-	-	-	-
V	23.7 ± 0.52	25.3 ± 0.78	160 ± 2.08	152 ± 11	-	-
Cr	8.24	13.7	136 ± 1	136 ± 4	178 ± 16	172 ± 8.5
Mn	13 ± 0.52	13.2 ± 0.46	316 ± 3.16	313 ± 5	920 ± 40	924 ± 18
Fe	7350 ± 110	7350 ± 250	40800 ± 408	40805 ± 1673	44800 ± 986	39926 ± 1200
Co	3.48 ± 0.2	3.91 ± 0.24	39.4 ± 0.4	39.4 ± 2.9	23 ± 1.3	19 ± 0.2
Ni	9.32 ± 0.51	10.5 ± 3.2	39.4 ± 0.39	39.4 ± 0.14	128 ± 8.96	23 ± 1
Zn	12.1 ± 1.29	11.2 ± 1.8	101 ± 1	101 ± 3	175 ± 13	148 ± 3
As	6.18 ± 0.27	6.25 ± 0.35	18.9 ± 0.2	18.9 ± 0.4	17.1 ± 5.13	17.5 ± 4
Se	1.33 ± 0.07	1.33 ± 0.09	0.78 ± 0.03	0.72 ± 0.3	1.59 ± 0.08	1.49 ± 0.1
Br	18.7 ± 0.39	17.9 ± 0.5	67 ± 7.97	70 ± 5	99.7±2.5	99.7±2.7
Rb	7.5 ± 0.3	7.5 ± 1.3	99.9 ± 8.49	102 ± 14	-	-
Sr	63.8 ± 1.4	63.4 ± 5.3	302 ± 3	302 ± 20	224.5 ± 67.3	200 ± 10
Mo	0.8 ± 0.24	0.79 ± 0.28	-	-	-	-
Sb	0.46 ± 0.03	0.46 ± 0.04	1.96 ± 0.04	1.96 ± 0.06	0.96 ± 0.05	0.74 ± 0.04
I[a]	-	-	-	-	-	-
Cs	0.59 ± 0.01	0.59 ± 0.02	6.4 ± 0.26	6.2 ± 0.06	7.8 ± 0.7	6.7 ± 0.08
Ba	41 ± 2	41 ± 3	268 ± 19	268 ± 12	-	-
La	-	-	33.7 ± 1.61	31 ± 5	27.8 ± 1	27.8 ± 1.1
Ce	11.9 ± 0.2	17.5 ± 3.6	64.5 ± 19.4	73.9 ± 1.5	56.7 ± 2	57 ± 3
Sm	1.08 ± 0.03	1.08 ± 0.04	-	-	4.66 ± 0.2	4.25 ± 0.5
Eu	0.12 ± 0.003	0.32 ± 0.1	1.18 ± 0.35	2.42 ± 0.04	1 ± 0.01	1.0 ± 0.1
Tb	-	-	0.696 ± 0.2	0.7 ± 0.03	0.68 ± 0.02	0.60 ± 0.02
Hf	0.59 ± 0.01	0.59 ± 0.05	3.66 ± 1.1	4.41 ± 0.08	-	-
Ta	-	-	1.03 ± 0.31	1.00 ± 0.02	0.88 ± 0.02	0.88 ± 0.02
Au	-	-	-	-	0.017 ± 0.005	0.017 ± 0.005
Th	1.4 ± 0.03	1.4 ± 0.04	9.8 ± 0.3	9.8 ± 0.3	10 ± 0.5	9.14 ± 0.09
U	0.51 ± 0.01	0.51 ± 0.02	2.45 ± 0.2	2.23 ± 0.2	2.26 ± 0.15	2.29 ± 0.3

[a] I concentration was determined using SRM 1515 (apple leaves): certified value 0.3 ± 0.09; determined value 0.26 ± 0.12..

Table 3. The average for 2013-2014 years elemental content of soils and bottom sediments (BS) for two different stations of Anapa region, upper continental crust (UCC) and average soils of the North Caucasus (SNC) (mean ± standard deviation, µg/g dry weight).

Element	Station 7		Station 2c		UCC [a]	SNC [b]
	Soils (*n* = 5)	BS (*n* = 2)	Soils (*n* = 8)	BS (*n* = 2)		
Na	4200 ± 700	4300 ± 700	8000 ± 2000	7400 ± 2200	24259	-
Mg	20000 ± 6300	10200 ± 5600	5300 ± 3000	5000 ± 3400	14957	-
Al	60000 ± 7000	38000 ± 600	23000 ± 2000	20000 ± 400	81505	-
Cl	260 ± 160	800 ± 300	430 ± 150	240 ± 70	370	-
K	16000 ± 3000	11200 ± 600	8300 ± 1400	8900 ± 2600	23244	-
Ca	44000 ± 6300	73000 ± 11000	68200 ± 10400	75300 ± 12100	25658	-
Sc	12.1 ± 3.5	7.8 ± 0.2	1.48 ± 0.30	1.46 ± 0.01	14	-
Ti	3500 ± 400	2400 ± 300	600 ± 180	450 ± 70	3897	5030
V	136 ± 18	88 ± 5	14 ± 6	11.5 ± 1.2	97	126
Cr	89 ± 25	86 ± 38	12 ± 4	9 ± 2	92	109
Mn	704 ± 116	463 ± 50	210 ± 50	180 ± 13	774	930
Fe	33500 ± 8600	34800 ± 8800	4900 ± 600	4800 ± 100	39176	-
Co	17.7 ± 5.1	15.0 ± 0.1	2.0 ± 0.3	1.9 ± 0.3	17.3	-
Ni	58.2 ± 19.2	53.1 ±7.8	5.3 ± 1.7	5.5 ± 0.4	47	47
Zn	86.3 ± 11.4	112 ± 51	19 ± 10	14 ± 3	67	106
As	14.8 ± 2.5	17.6 ± 5.1	6.7 ± 0.7	6.5 ± 0.4	4.8	-
Se	1.1 ± 0.9	1.6 ± 1.5	0.20 ± 0.15	0.2 ± 0.1	0.09	-
Br	18.6 ± 4.9	17.3 ± 1.1	3.5 ± 0.7	2.7 ± 0.6	1.6	-
Rb	83.3 ± 21.9	53.8 ± 3.3	27.9 ± 4.5	25.9 ± 0.1	84	-
Sr	370 ± 250	438 ± 49	470 ± 170	500 ± 4	320	216
Mo	6.2 ± 5.3	14.2 ± 14.1	1.0 ± 1.0	1.0 ± 0.1	1.1	-
Sb	1.7 ± 0.4	2.4 ± 0.9	0.20 ± 0.03	0.17 ± 0.01	0.4	-
I	12.3 ± 2.7	16.5 ± 3.2	2.1 ± 0.7	4.5 ± 0.9	1.4	-
Cs	5.5 ± 1.7	3.3 ± 0.04	0.40 ± 0.07	0.40 ± 0.01	4.9	-
Ba	530 ± 170	524 ± 84	225 ± 60	200 ± 41	624	720
La	36.5 ± 18.6	66.9 ± 55.3	10.8 ± 8.2	10.8 ± 6.4	31	-
Ce	41.9 ± 24.5	39.6 ± 6.8	11.5 ± 2.7	13.7 ± 0.4	63	-
Sm	5.6 ± 1.8	9.8 ± 7.4	1.2 ± 0.4	1.3 ± 0.3	4.7	-
Eu	1.7 ± 0.6	0.8 ± 0.9	0.3 ± 0.1	0.30 ± 0.01	1	-
Tb	0.6 ± 0.2	0.6 ± 0.04	0.14 ± 0.03	0.140 ± 0.004	0.7	-
Hf	6.1 ± 1.9	4.3 ± 1.1	1.2 ± 0.3	1.1 ± 0.2	5.3	-
Ta	0.6 ± 0.2	0.5 ± 0.1	0.10 ± 0.03	0.09 ± 0.01	0.9	-
Au	0.01 ± 0.001	0.01 ± 0.001	0.002 ± 0.002	0.002 ± 0.001	1.5	-
Th	8.6 ± 2.1	7.6 ± 0.3	1.4 ± 0.3	1.27 ± 0.02	10.5	-
U	4.3 ± 6.5	2.2 ± 0.8	0.5 ± 0.1	0.440 ± 0.002	2.7	-

[a] elements in the average UCC according to [41], [b] elements in soils of the North Caucasus according to [43].

For a better description of the local conditions for each sampling site, we determined the content of the same elements in soil as well as in sediments. This procedure were used for a more complete analysis of the distribution of elemental content of all considered elements in plants, soil and sediments collected from the Anapa region. In that case, standard deviations reflected the variability of values based on sets of samples.

Besides the above mentioned statistical analysis techniques, we have also used some graphic analysis procedure such as the ternary diagrams. They allowed revealing at which extent the content of Cl, Br and I could be used to discriminate the different species of studied plants. All computations were performed using the Libre Office 5.0.2 and Past 3.0 [42] as well as OriginTM 8, Statsoft StatisticaTM 11.

3. Results and Discussion

3.1. Accumulation of Elements in Soils and Bottom Sediments

The levels of the minor and trace elements in soils and sediments from two stations located at 1 km (station 7) and 4 km (station 2c) from the city dump is given in **Table 3** where you can see the statistical stability of the data as well. The content of the same elements in the average UCC [41] and the levels of some elements in soils of the North Caucasus [43] are listed.

The average values from 2013-2014 years were calculated from two different sets of data. Standard deviations reflected the variability of values through neutron activation analysis of samples.

The determined concentrations of the majority of elements in soils and BS for each station belonged to close ranges. In that case, we would contemplate these milieus for plants as one. For further analysis, the average values were calculated as arithmetic means for soils (data from surface and from 0 - 20, 20 - 40, 40 - 60 cm layers) and bottom sediments (only from surface). The standard deviation for joint is given on the **Figure 2**.

As follows from **Table 3**, Se, Br, and I concentrations in soils and BS from both stations (**Figure 2**) are higher than in UCC. It can be explained by the loca-

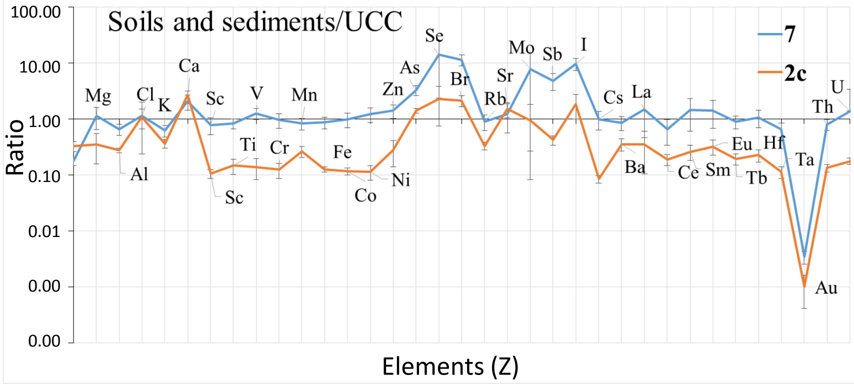

Figure 2. The diagram of the elemental content in soils and sediments normalized on UCC for 7 and 2c stations.

tion of Anapa region near the sea and the fact that atmospheric supply from the marine environment is the predominant source of these elements in the soil [44] [45]. As described in [46] [47] soil contamination may be considered when concentrations of an element in soils were two-to three times greater than the mean background levels. For our study station 7 (the closest to city dump) hypothetically was the most polluted and the station 2c which situated on the shore was used as background for whole transect. The increasing levels of As, Mo, and Sb in soils and BS from the most polluted station 7 probably indicates the anthropogenic pollution with these elements. Increasing trend of levels of elements from the relatively pristine to polluted area probably ensue from influences of local disposal dump and traffic impacts.

The concentrations of all elements (except for V and Ni) reported by Dyachenko *et al.* [43] for the soils of the North Caucasus are higher than those determined in the soil samples from the most polluted station 7 near city dump of Anapa.

Our data were also compared to results of [48] who determined in laboratory conditions the levels of several elements for non-polluted, low polluted and moderate polluted soil from the Southern part of Russia using the integral index of biological state of soil (**Table 4**). It helps to realize the level of local differences in elemental content of soils from the standard levels for whole region.

The maximal concentrations of Cr, Zn, As, Se and Sr in soils of Anapa region that were determined at the stations 6 and 7 (the nearest to city dump) are similar with the values reported for moderate polluted soils. Nevertheless all median

Table 4. Maximal and median elemental concentrations (μg/g dry weight) in soils from Anapa region (our data) and values for non-polluted and polluted soils from the Southern part of Russia.

Element	Soils in Anapa region (*n* = 40)		Soils in the Southern part of Russia[a]		
	Max	Median	Non-polluted	Low polluted	Moderate polluted
V	150	30	<200	200 - 300	300 - 850
Cr	**105**	30	<70	70 - 90	90 - 170
Mn	900	370	<1000	1000 - 1600	1600 - 1800
Co	24	4	<18	18 - 36	36 - 250
Ni	80	12	<50	50 - 100	100 - 700
Zn	**270**	50	<125	125 - 200	200 - 850
As	**36.8**	7.1	<17	17 - 30	30 - 160
Se	**2.31**	0.25	<0.7	0.7 - 1.4	1.4 - 9
Sr	**840**	510	<250	240 - 450	450 - 3200
Mo	15.7	1.1	<8	8- 400	>400
Sb	2.1	0.6	<5	5 - 12	12-200
Ba	690	250	<900	900 - 1500	1500 - 4000

[a] elements in soil according to [48]. The concentration of elements which relate to moderate polluted range are given in bold.

values of studied elements (except for Sr) in soils of Anapa region are within the range of concentrations determined for non-polluted soils (**Table 4**) and less than maximum permissible levels of elements established in different countries (**Table 5**) [49]. Data of maximum permissible levels is widely used for ecological management in assessment of environmental impacts. It was concluded that the soils in study region were in low-polluted state despite the sources of anthropogenic stress.

3.2. Accumulation and Compartmentalization of Elements in Water and Coastal-Aquatic Plants

The data about accumulation of elements in different organs of plants were analyzed at the all stations, but after that, the average levels of elemental concentrations for whole Anapa region were calculated as arithmetic mean values obtained from all sampling stations. It helped to realize the ability of different species of plants to reflect the chemical features of environment, including the local pollution influences.

The concentrations of all elements determined (except for K and Cl) are higher in roots of *P. australis* than in leaves. In particular, the leaf/root ratios range from 0.86 for Br to 0.05 for Co (**Figure 3**). For Sc, V, Fe, Co, I, Cs, Sm and Th the root concentrations are one order of magnitude higher than concentrations in leaf. The obtained results confirm the data that *Phragmites australis* is prevalently a root bioaccumulator species [11] [13] [15] [20]. It is well known that roots are generally the main pathway of trace elements to plants. However, other tissues of *P. australis*, in particular, leaves, show the ability readily to translocate such elements as Na, Ti, Zn, Br, and Sr [15].

In contrast to *P. australis*, the concentrations of all elements, except for Fe, Se, Mo, Eu and U are higher in leaves of *Carex conescens* than in roots (**Figure 3**). Our results emphasized the differences between accumulation features of these

Table 5. Maximum permissible levels of elements in soils established in different countries.

Element	Original data ($n = 40$)			Russia	Germany	Netherlands	USA	Finland
	min	max	median	[48]		[49]		
V	10	150	30	150	-	-	-	100
Cr	6	105	30	90	100	250	1000	100
Mn	150	900	370	1500	-	-	-	-
Co	1.6	24	4	-	50	50	-	20
Ni	3	80	12	85	100	100	-	50
Zn	6	270	50	100	300	500	2500	200
As	3	36.8	7	2	50	30	30	5
Se	0.06	2.31	0.25	-	10	-	-	-
Mo	0.2	15.7	1.1	-	10	40	-	-
Sb	0.1	2.1	0.6	4.5	-	-	-	2
Ba	150	690	250	-	-	400	-	-

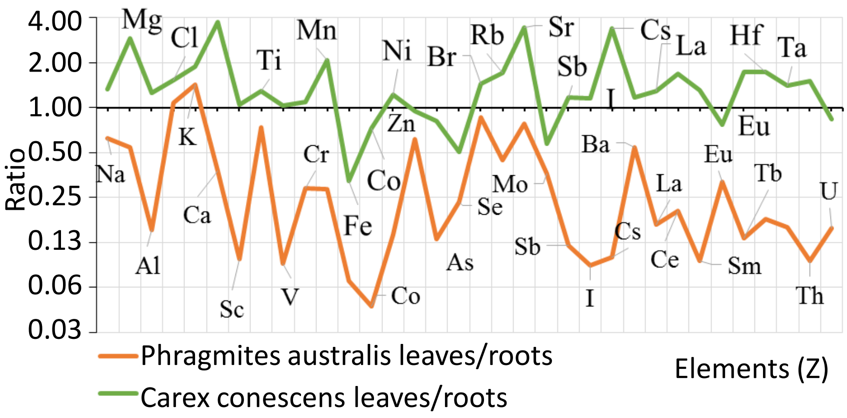

Figure 3. Average differences between leaves/roots ratios for *Phragmites australis* and *Carex conescens*.

two species. The *Carex conescens* could be used as a good bioconcentrator of majority of elements from soils and bottom sediments but *P. australis* could be used as a good comparative biomonitor (root type) in clean and polluted areas due to its self-cleaning processes.

The obtained results were compared to the available data for *Phragmites*, *Carex*, and *Cladophora*, reported by other authors (**Table 6**) to represent the variability of concentrations in different regions. The concentrations of most elements in leaves and roots of *Phragmites australis* sampled in the mountain lake in Italy [20] and in the mouth of the longest Sicilian river [15] [20] are higher compared to our results. The exceptions are Ti, Mn, As, Sb and Ti, V, As, Se, which values in roots and leaves, respectively, are higher in the present study. The values of Co, Zn, Rb, and Th in *Carex pendula* sampled in Germany in botanical garden [26] are higher than our data; the reverse trend is observed for Sc, Cr, Fe and Cs. The elemental content of *Cladophora* reported by different authors varies in a wide range depending on the sampling region and the species. Thus, the levels of Mg, Ca and Mn in *Cladophora glomerata* from the lake Karasevoe in Siberia are one order of magnitude higher compared to our results [51]. In contrast, the content of Ca, Co and Ni in *Cladophora sp.* from the Baltic Sea [52] is one order of magnitude lower than those determined in the present study. The levels of Fe and Zn in *Cladophora glomerata* sampled in the Danube river [53] are 2-fold higher than our data. Thus, the exact concentrations of elements in studied species are absent or not widely available. As a result, it is necessary to determine the range of variability in different pollution conditions.

According to the wide variability of elemental content of studied plants across the regions we normalized our data on values for so called reference plant for comparative analysis. The results of normalized elemental concentrations against Reference Plant (RP) show that roots and leaves of *P. australis* are good accumulators of Na, Ti, and Br and, in contrast, contain lower levels of Zn, Rb, and Ba than RP (**Figure 4**). In *Carex* roots and leaves the levels of Na, Ti, As, Th, and U are one order of magnitude higher than in RP. In contrast, Mg, K, Mn,

Table 6. Elemental content of different species of *Phragmites*, *Carex* and *Cladophora* ($\mu g \cdot g^{-1}$ dry weight).

El.	*Phragmites australis*			*Carex pendula*	*Cladophora sp.*	*Cladophora glomerata*	
	Roots[a]	Roots[b,c]	Leaves[b,c]	Whole plant[d]	Whole plant[e]	Whole plant[f]	Whole plant[g]
Na	–	–	17100	17100	17100	–	3000
Mg	1550	–	7800	7800	7800	–	23000
Al	–	3153	–	–	–	–	–
K	17000	–	24500	24500	24500	–	11000
Ca	–	–	8500	8500	8500	–	170000
Sc	–	–	–	–	–	–	–
Ti	–	<0.05	–	–	–	–	–
V	14.5	9.2	–	–	–	–	–
Cr	3.06	6.97	–	–	–	–	–
Mn	300	475.8	470	470	470	500	18000
Fe	2990	5561	2400	2400	2400	10000	2300
Co	–	8.0	0.5	0.5	0.5	–	–
Ni	6.52	9.12	3.1	3.1	3.1	–	6.3
Zn	54	104	60	60	60	200	–
As	–	<0.05	–	–	–	–	5
Se	–	<0.5	–	–	–	–	–
Rb	–	–	–	–	–	–	–
Sr	–	48.5	90	90	90	–	–
Mo	–	16.8	–	–	–	–	–
Sb	–	<0.05	–	–	–	–	–
Cs	–	–	–	–	–	–	–
Ba	–	47.3	–	–	–	–	–
Th	–	–	–	–	–	–	–

[a] [20], [b] [15], [c] [49], [d] [26], [e] [52], [f] [53], [g] [51].

Zn, Rb, Cs, and Ba show lower levels in comparison to RP concentrations (**Figure 4**). The concentrations of the majority of elements in algae *Cladophora* are at least one order of magnitude higher than in RP. The levels of Zn and Rb, that are lower than RP concentrations, become the exception (**Figure 4**).

The different composition of *Phragmites australis* and *Carex conescens* with *Cladophora sericea* is explainable by fully different uptake mechanisms of elements either by all surface of plant from water (*Cladophora*) or by roots (*Phragmites* and *Carex*). In addition, some elements may characterize the different types of plants (for example, algae). Thus, the level of As, that is a part of phosphatides in algae and plays an important role in glycometabolism [54], is 140-fold higher in *Cladophora* than its concentration in RP (**Figure 4**).

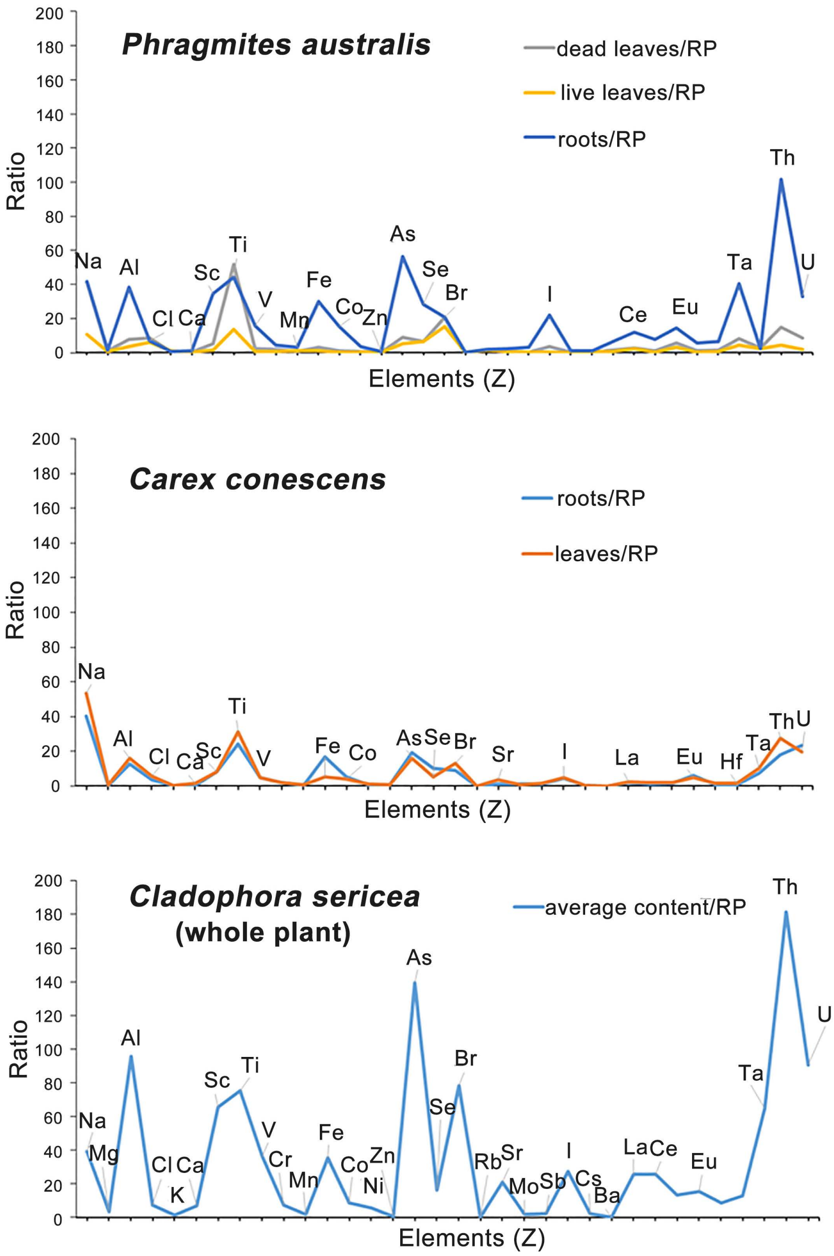

Figure 4. Studied plant/Reference plant ratios for different parts of *Phragmites australis*, *Carex conescens* and *Cladophora sericea*.

The similar patterns of elemental accumulation for all three species are found for several elements. Thus, the levels of Na, Ti and Br are higher than in RP; the reverse trend is revealed for Zn and Rb. It could be explained by abundance or lower concentrations of mentioned elements in the surrounding environment (soils, BS).

3.3. Transport of Minor and Trace Elements from Bottom Sediments to Plants

The element distributions between the two compartments follow the order: bottom sediment > plant due to differences in concentrations. The differences between species accumulation with taking into account the type of accumulation (roots for *P. australis* and live leaves for *C. conescens*) were represented by normalizing concentrations of elements in plants from the same station (2c) on values in bottom sediments (**Figure 5**). BS was used as a milieu, which at the same station reflects the local elemental fingerprint of water and other components.

It is known that most rooted macrophytes uptake chemicals primarily from sediment pore water [15], but it is also reported that some rooted submersed plants may absorb metals directly from water when they are not readily available in sediments and/or in high concentrations in the surroundings [55]. The one more way of coming the elements to plants is an uptake mechanism of them from air. Plants may absorb Cl, Br, and I directly from the atmosphere; and the marine environment is the main source of these halogens for plants [45] [53].

It is found that the levels of Br and I in algae *Cladophora* are higher than in *Phragmites* and *Carex* (**Figure 4**). Our results are in agreement with the statement that algae are one of the best accumulators of these elements [56].

To reveal the differences of halogens accumulation in *Phragmites*, *Carex* and *Cladophora* the ternary diagram for the levels of Cl (Cl/10), Br and I in plants normalized against content of these elements in sediments is built (**Figure 6**). After that for ternary diagram the values was proportionally reduced to relative units (by using OriginTM 8). *Phragmites* is characterized by high levels of Cl at the majority of sampling sites. In *Carex* the content of Br is equal at all stations except one. *Cladophora* is characterized by high levels of Br and I, while the content of Cl is the minimal. These results demonstrate the specific accumulation features of plants. For example *Cladophora* sericea accumulates Cl in small relative amounts in comparison to Br and I. *Phragmites australis* in the major cases selects I and Cl regardless Br. In that sense the *Carex conescens* demonstrates the most flexible ability for accumulation of these halogens.

4. Conclusions

- The similarity in elemental concentration in soils and sediments at the majority of sampling stations is established (**Table 3**). Sediments act as the primary source of elements for water plants. Regarding Cl, Br and I, the atmospheric supply from the marine environment is the predominant source. The concentration of majority of elements in soils of Anapa region are corresponded to values reported for non-polluted zones. The exceptions are the most polluted stations (6 and 7) near city dump, where elemental levels are several times higher if compared to median values.
- The study shows that *Phragmites australis* is prevalently a root bioaccumulator species; in contrast, the concentrations of all elements except for Fe, Se and Mo are higher in leaves of *Carex conescens* than in roots.
- The different composition of *Cladophora sericea* and *Phragmites australis-with Carex conescens* is explainable by different elemental uptake, either mainly by entire surface of plant from water (*Cladophora*) or by roots from sediments (*Phragmites australis* and *Carex conescens*).

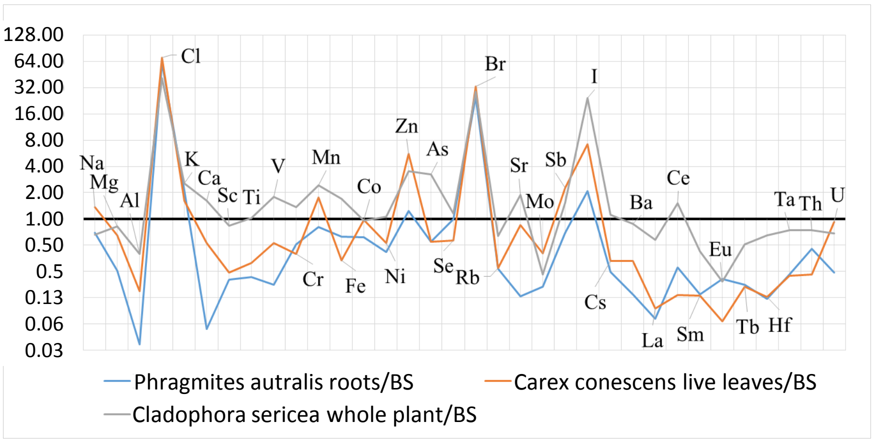

Figure 5. The elemental content of *Phragmites australis*, *Carex conescens* and *Cladophora sericea* normalized against bottom sediments (station 2c).

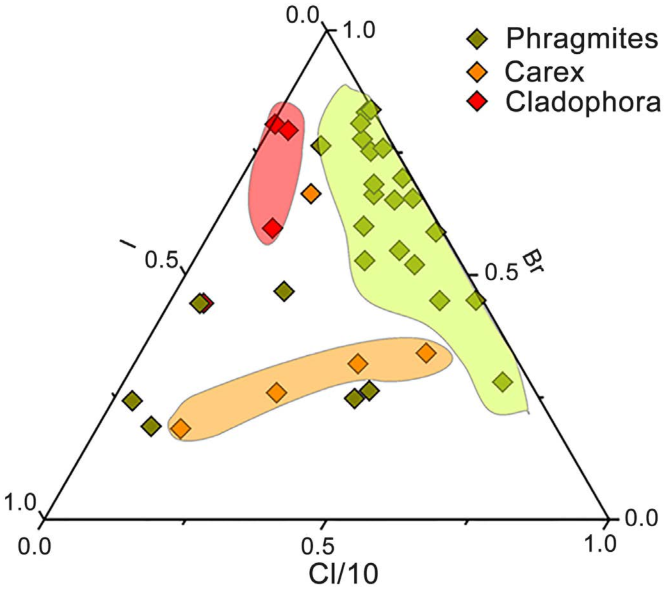

Figure 6. Ternary diagram for concentrations of Cl (Cl/10), Br and I for *Phragmites australis*, *Carex conescens* and *Cladophora sericea* normalized against content of these elements in sediments (BS). With some exceptions (*Phragmites samples*), all other points form three distinct clusters corresponding to each type of plant.

- Translocation of elements varies depending on the physiological property of elemental uptake and is generally more intense through plant tissues than from sediments to plants. Leaves of *Phragmites australis* show the ability to translocate such elements as Na, Ti, Zn, Br, and Sr. Among the determined elements the highest translocation between roots and leaves of *Carex conescens* is found for Sc, V, Cr, and Zn.
- The results of normalized elemental concentrations against Reference Plant show that roots and leaves of *Phragmites australis* are good accumulators of Na, Ti, and Br and, in contrast, contain lower levels of Zn, Rb, and Ba than RP. In *Carex conescens* roots and leaves the levels of Na, Ti, As, Th, and U

are one order of magnitude higher than in RP. In contrast, Mg, K, Mn, Zn, Rb, Cs, and Ba show lower levels in comparison to RP concentrations. The concentrations of the majority of elements in algae *Cladophora sericea*. are at least one order of magnitude higher than in RP.

- *Cladophora sericea* accumulated Cl in small relative amounts in comparison to Br and I. *Phragmites australis* in the major cases selected I and Cl regardless Br. In that sense the *Carex conescens* demonstrated the most flexible ability for accumulation of these halogens.
- The found ratios BS to plants demonstated the different ability of this three species to reflect the local elemental fingerprints. The levels of majority of elements in *Phragmites australis*, *Carex conescens*, *Cladophorasericea* could be used in future biomonitoring studies on local and regional scales. These plants are potentially useful for monitoring of pollution in general, and for the most elements examined in particular.

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