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# Quantitative Analyses of Chemical Elements in *Phragmites australis* as Bioindication of Anthropization in Urban Lakes

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**Abstract:** Urban areas face numerous provocations, such as air, water, and soil contamination. Additionally, urban lakes have numerous beneficial services that contribute to urban sustainability. In urban aquatic ecosystems, X-ray fluorescence can provide complex answers regarding the presence of elements associated with environmental risk. The study aimed to screen the elements with different potentials (critical raw materials—CRMs; toxic; potentially toxic) from *Phragmites australis* leaves along the Colentina urban river. The samples from the peri-urban and urban river courses highlighted the presence of elements with different potentials for ecosystems and human health. The investigated stations were influenced by regional anthropogenic pressures, where *P. australis* highlighted the absorption of the dominant elements found in the environment. From the total of 56 elements present in the samples, some have structural roles (K, Si, Ca, and Cl), some are from the CRM category, and some are airborne heavy metals and rare metals. Furthermore, among CRMs, cesium, lanthanum, magnesium, phosphorus, vanadium, sulfur, holmium, and titanium were recorded with higher values. Although the values of the elements in the anthropogenic source were in low concentrations, spatial differences were highlighted. The stations in agricultural areas were different from the peri-urban and urban ones.

**Keywords:** anthropogenic impact; common reeds; XRF; CRM; toxic element; urban

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**Citation:** Catana, R.D.; Podosu, A.; Florescu, L.I.; Mihai, R.A.; Enache, M.; Cojoc, R.; Moldoveanu, M. Quantitative Analyses of Chemical Elements in *Phragmites australis* as Bioindication of Anthropization in Urban Lakes. *Sustainability* **2023**, *15*, 553. https://doi.org/10.3390/su15010553

Academic Editors: Małgorzata Szczesio, Anna Turek and Kinga Wieczorek

Received: 28 November 2022
Revised: 20 December 2022
Accepted: 23 December 2022
Published: 28 December 2022

## 1. Introduction

In recent times, natural environments have been intensely subjected to different forms of pollution. The development of the human community involved urbanization, industrialization, and heavy traffic that led to environmental contamination, exposed urban residents to serious risks, and profoundly affected the services that ecosystems can provide [1]. The urbanization process on rivers is expressed by increased contaminants and nutrient quantities, which alter the river morphology [2]. For example, heavy metals from various sources (the combustion of coal, fuel, household waste, industrial processes, etc.) are airborne and mobilized with other particles (which may contain soot, chromium, manganese, lead, cadmium, iron oxides, etc.) from the soil surface and scattered at a distance [3]. In previous research, there was interest in critical raw materials (CRMs) (all rare earth elements and platinum group metals, or PGMs), which represent those raw materials linked to all industries: green technology, telecommunications, space exploration, medical devices, micro-electronics, transportation, defense, etc. Additionally, CRM sources are classified as primary (including ores, concentrates, processed, or refined materials) and secondary (waste recycling), both of them having high importance and attention [4]. The interactions among elements in water, soil, and organisms can cause major changes in the quality of life on Earth [5]. Worldwide, there have been stable limits on concentrations and laws governing quality standards for heavy metals (known to be problematic for human health) [6] and for pesticides and insecticides used in agriculture [7]. However, many elements' effects are still unknown or less discussed.

In big cities, such as Bucharest, the sources of the ecotoxic elements are diverse, represented by the negligence of selective garbage management, derelict trash in isolated areas and near the lakeshore, road traffic emissions, agricultural and domestic toxic compounds, deposition of dust and aerosols, and other anthropogenic activities.

The Romanian capital, Bucharest, is crossed in the north by the Colentina River, which contains 15 basins with different services: recreation, fishing, flow regulation, landscape, etc. The river receives wastewater from the northern area, which is discharged from the sewerage system of Buftea City [8]. The principal stresses on the lakes are pollution, car traffic, land destination changes, expansion of road infrastructure, and illegal waste incineration. Further, the impacts on the area consist of declining aquatic life, chaotic real estate development, water pollution, and soil degradation.

The lakes of the Colentina River are invaded especially by communities formed by *Phragmites australis* (Cav.) Trin. ex Steud, *Typha angustifolia* L., and *Typha latifolia* L. The accumulation of pollutants by plants is used to monitor the impact of activities (municipal and industrial wastewater disposal, leaks from agriculture) [9,10]. *Phragmites* sp. is a widespread species that grows in different living environments, resisting extreme environmental conditions [11] and gaining an invasive character [12]. It has been found that *P. australis* can accumulate heavy metals in the rhizomes and stems [13], and the stems and leaves are rich in micro- and macronutrients [14]. *P. australis* is a particularly important level of primary producer in ecological systems and an important component that can contribute to depollution processes due to its possibility to absorb mineral ions through roots at very low concentrations, making this process very efficient [15].

The aim of the study was to assess the elements with different potentials in aquatic areas of Bucharest via *P. australis* leaves. The objectives were to determine the content of the elements in *P. australis* leaves (1) and to identify the hotspots of anthropogenic pressures as potential sources of the toxic elements (2).

## 2. Materials and Methods

### 2.1. Study Area

The geological characteristics of the Bucharest city area are exclusively represented by Quaternary deposits: alluvial-proluvial and diluvial categories. The aluvial-proluvial soil contains clay and sandy yellow dust, with loess and diluvial dolls of a loess-like type and clay with a slightly macroporous structure [16]. The superficial layer is anthropogenic. The unit of the Colentina River area has a thickness of 5–25 m and is composed of sand and gravel. The intermediate deposits are of clay origin, with a depth of 15–30 m and a thickness of 2–18 m [17,18].

The study was carried out in 2019, along the Colentina River, 7 stations were established: 3 stations in river areas (station 0—upstream at the entrance to Bucharest; station 1—Crevedia Branch; and station 6—after Cernica's shuttles, downstream whether the river exits the city); and 4 stations in the lake chain (in the upstream to downstream order: station 2 in Mogoșoaia Lake, stations 3 and 4 in Fundeni Lake, and station 5 in Cernica (Figure 1). The stations were established according to the presence of *P. australis*.

### 2.2. Field Sampling and Laboratory Analysis

The sampling of *P. australis* was taken in the month of July. The leaves were collected from 1.50 m above the water by three young individuals from each station. The 40 g plant wet samples were dried in ovens for 2 h at 60 °C, followed by mechanically powdering using a porcelain mortar and pestle. Further, 20 g dry samples were calcined in the Nabertherm LE 6/11/B150 compact muffle furnace for 2 h at 220 °C to remove the organic component.

An X-ray fluorescence system (XRF Rigaku ZSX100e, Supermini model) analytical technique with a wavelength dispersion has been performed for elemental composition determination. Further, a pulse height analysis (PHA) adjustment was carried out once a day, after the initialization of the instrument. The adjustment was performed for each of the detectors (F-PC and SC) using the PHA adjustment sample.

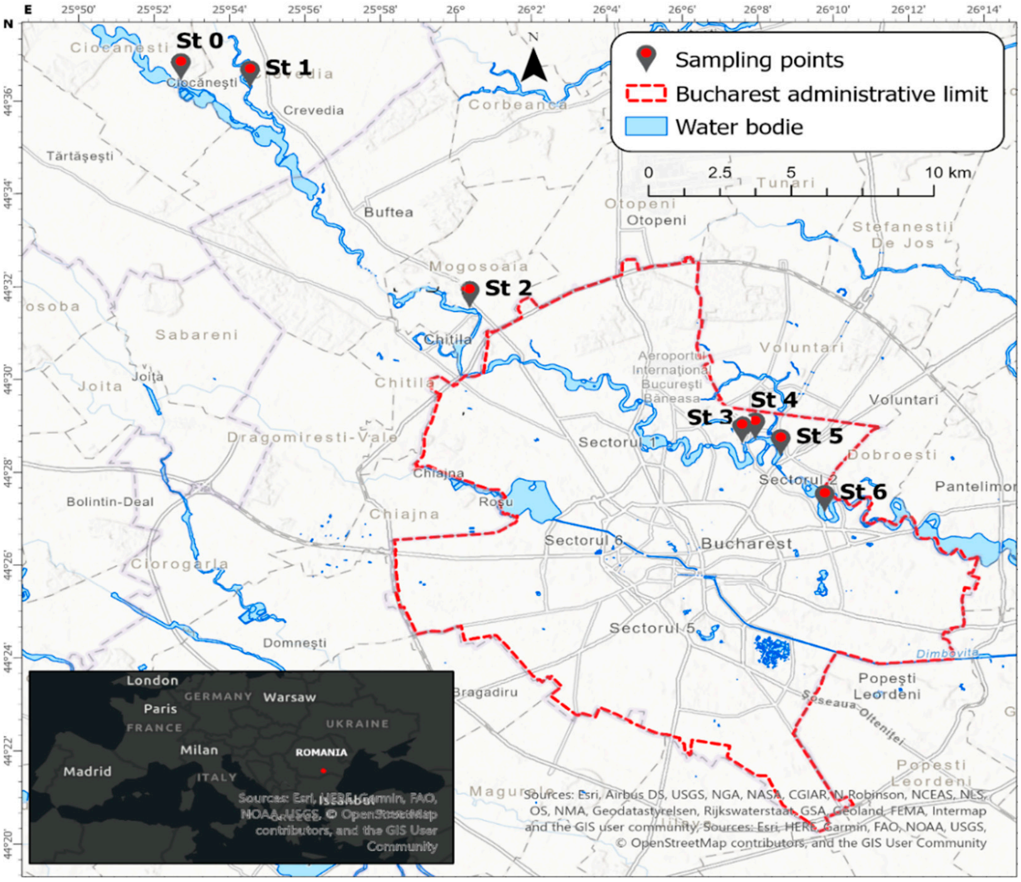

**Figure 1.** The map of the Colentina River with the sampling stations (the red dots represent the limits of Bucharest). (Sources: Esri, HERE, Garmin, FAO, NOAA, USGS, ©OpenStreetMap contributors, and the GIS User Community).

The method used SQX software to make qualitative analyses and calculate semiquantitative analysis values without using standard samples (SQX analysis). In the SQX analysis, a library sample with a composition most similar to an analysis sample is automatically retrieved for more accurate analyses.

The material analysis mode of the XRF spectrometer is capable of a wide range of material analysis, from aluminum ($Z = 13$) to uranium ($Z = 92$). Material compositions ranging from 0.1% to 100% can be detected accurately.

It can also be used for microsamples, thin samples, aerosols, and liquids, with detection limits of 2–20 $\text{ng/cm}^2$ for most elements.

One gram of the vegetable ash was fixed in the sample cells with a 30 mm readable diameter, covered on both sides with polypropylene foil of 6 µm thickness from Rigaku, and fixed with a Snap-On ring. The principle of the method consists of irradiating the sample with an X-ray and reading the theta angle formed by the reflected wave, which is specific to each element in the periodic table [18]. The software converts the intensity peak into a mass percentage for quantitative analyses. The results are generated in the elemental oxide weight percentage (wt %) [19]. The conversion from the percentage values (generated by XRF analysis) into absolute values was performed by calculating the element percent from the element oxide and further processing the ash percent of the oxide (at 1 g ash) expressed in mg $\text{kg}^{-1}$/dry weight [20].

The elements identified through XRF analysis were grouped into critical raw materials (CRMs), heavy metals (HM), and other elements (OE). Additionally, there was the presence of rare metals.

### 2.3. Data Analysis

The boxplot is a graphical method based on descriptive statistics with a summary displaying the minimum, the maximum, the sample median, the mean, the first and third quartiles, and outliers. Furthermore, the distribution, symmetry, and outliers of the data can be visualized [21]. The discriminant analysis (DA) represents a multivariate technique for isolating more groups of observations based on variables measured on each sample and finding the contribution of each variable. Additionally, using different data from various sites, the DA can find the pattern within the data and classify it effectively [22]. Agglomerative hierarchical clustering (AHC) is a widely used method to partition a large data set into N clusters based on the similarity of objects within clusters and differences between clusters [23]. In the AHC and DA analyses, all the elements identified in the XRF determination were used. The statistical analysis was performed with XLSTAT Pro (2013) [24].

## 3. Results

The XRF results showed the presence of 56 elements in *P. australis* samples, which varied between (0.0011–21.852 mg kg$^{-1}$), with a close occurrence among stations (Table 1). The number of elements/stations varied between 30 (stations 3 and 4) and 36 (station 1).

In considering all the elements presented in the research, the following were accidental: Au, Ce, Er, Ho, Ir, La, Nb, Ta, Tb, Tl, W, Yb, Zr, Bi, Dy, Hg, Nd, Pm, Pt, Sm, and Tm. The highest concentrations belonged to the elements with structural importance for plants, such as potassium (K), silicon (Si), calcium (Ca), and chlorine (Cl) (Table 1). Several elements caught our attention because of their higher concentrations: barium (Ba) (0.32 mg kg$^{-1}$), molybdenum (Mo) (0.13 mg kg$^{-1}$), or their frequency of incidence: silver (Ag) and aluminum (Al).

In addition to the identified elements in *P. australis* ash, there is also the presence of 25 elements that are part of the CRM category. The elements phosphorus, magnesium, titanium, and vanadium were the most represented elements in the CRMs list, while strontium, hafnium, cobalt, tungsten, germanium, thallium, gallium, bismuth, and niobium were found in lower concentrations (Table 1 and Figure 2). The CRM elements from the category of Platinum Group Metals (PGMs) and REEs (both HREE and LREE) were also found in the *P. australis* ash samples (Figure 3). Iridium (Ir) and platinum (Pt) were isolated at low concentrations. Similarly, the REEs were randomly encountered along the river course (Table 1). It was observed that lanthanum (La), cerium (Ce), and holmium (Ho) had higher concentrations compared to the other elements in the REE list (Figure 2).

The category of heavy metals that are specified in the European Directives (1999/30/EC, 2004/107/EC, and 2008/50/EC) for ambient air quality monitoring, arsenic (As) (0.022 mg kg$^{-1}$), lead (Pb) (0.017 mg kg$^{-1}$), Ni (0.02), and mercury (Hg) (0.003 mg kg$^{-1}$) were assimilated by plants (Table 1, Figure 2).

The discriminant analysis, based on the CRMs, HMs, and OE elements, offers a better understanding of the contribution in the *P. australis* ash samples through the differentiation between groups. Regarding the CRMs, the generated ellipse is evidently a scatter, from the point of view of the higher concentrations of the elements. Thus, caesium (Ce), lanthanum (La), magnesium (Mg), phosphorus (P), vanadium (V), sulfur (S), holmium (Ho), and titanium (Ti), noted for their higher values, made an important contribution to the group. HM represented the group of elements whose concentrations were reduced compared to the other two categories, thus being highlighted by the small ellipse in the analysis. The largest ellipse belonged to the other elements group, which had the greatest diversity both in elements and concentrations. However, in addition to the major elements such as macrominerals calcium (Ca), chlorine (Cl), silicon (Si), potassium (K), and mangan (Mn), other less common elements such as silver (Ag), molybdenum (Mo), barium (Ba), and rhenium (Re) were also noted (Figure 3).

**Table 1.** Descriptive statistics (mean and SD—standard deviation) and presence/absence of elements (mg kg$^{-1}$) determined by XRF analysis in *P. australis* from the studied sites.

| | **Elements** | | **Mean ± SD** | **Station 0** | **Station 1** | **Station 2** | **Station 3** | **Station 4** | **Station 5** | **Station 6** |
|---|---|---|---|---|---|---|---|---|---|---|
| CRMs | Bismuth | Bi | 0.002 ± 0.005 | + | | | | | | |
| | Cerium | Ce | 0.105 ± 0.185 | | | | + | | + | |
| | Cobalt | Co | 0.016 ± 0.023 | + | + | | | + | | |
| | Dysprosium | Dy | 0.011 ± 0.029 | + | | | | | | |
| | Erbium | Er | 0.017 ± 0.03 | | | | | | + | + |
| | Gallium | Ga | 0.005 ± 0.006 | | + | + | + | | + | |
| | Germanium | Ge | 0.011 ± 0.01 | + | + | + | + | | + | |
| | Hafnium | Hf | 0.023 ± 0.031 | | | | | + | + | + |
| | Holmium | Ho | 0.035 ± 0.062 | | | + | | + | | |
| | Lanthanum | La | 0.12 ± 0.215 | | | | + | | | + |
| | Lutetium | Lu | 0.014 ± 0.018 | | | + | | | + | + |
| | Magnesium | Mg | 0.373 ± 0.235 | + | + | + | + | + | + | + |
| | Niobium | Nb | 0.001 ± 0.001 | | + | | | | + | |
| | Neodymium | Nd | 0.042 ± 0.112 | | | | | | | + |
| | Phosphorus | P | 2.109 ± 0.401 | + | + | + | + | + | + | + |
| | Promethium | Pm | 0.031 ± 0.084 | | + | | | | | |
| | Samarium | Sm | 0.024 ± 0.065 | | | + | | | | |
| | Strontium | Sr | 0.087 ± 0.033 | + | + | + | + | + | + | + |
| | Tantalum | Ta | 0.009 ± 0.016 | | | + | | + | | |
| | Thallium | Tl | 0.008 ± 0.013 | | | + | | | + | |
| | Thulium | Tm | 0.006 ± 0.016 | | | + | | | | |
| | Terbium | Tb | 0.029 ± 0.05 | + | | | + | | | |
| | Titanium | Ti | 0.163 ± 0.217 | + | + | + | + | | | |
| | Tungsten | W | 0.012 ± 0.021 | | | + | | + | | |
| | Vanadium | V | 0.145 ± 0.111 | + | + | + | + | + | + | + |
| | Yttrium | Y | 0.005 ± 0.008 | + | + | | | + | | |
| | Ytterbium | Yb | 0.012 ± 0.026 | | | | | | + | + |
| Platinum Group Metals | Platinum | Pt | 0.003 ± 0.008 | | | | + | | | |
| | Iridium | Ir | 0.005 ± 0.009 | | + | + | | | | |
| Rare metals | Silver | Ag | 0.118 ± 0.033 | + | + | + | + | + | + | + |
| | Gold | Au | 0.006 ± 0.01 | | + | | | | + | |
| Heavy metals | Lead | Pb | 0.017 ± 0.022 | + | | + | | | | + |
| | Arsenic | As | 0.022 ± 0.019 | + | + | + | + | + | + | + |
| | Nickel | Ni | 0.02 ± 0.015 | | + | + | + | + | | + |
| | Mercury | Hg | 0.003 ± 0.01 | | + | | | | | |
| Other | Calcium | Ca | 13.216 ± 3.098 | + | + | + | + | + | + | + |
| | Potassium | K | 21.852 ± 3.004 | + | + | + | + | + | + | + |
| | Chlorine | Cl | 7.023 ± 2.336 | + | + | + | + | + | + | + |
| | Sulfur | S | 2.156 ± 0.918 | + | + | + | + | + | + | + |
| | Iron | Fe | 0.258 ± 0.064 | + | + | + | + | + | + | + |
| | Mangan | Mn | 0.832 ± 0.517 | + | + | + | + | + | + | + |
| | Zinc | Zn | 0.044 ± 0.019 | + | + | + | + | + | + | + |
| | Copper | Cu | 0.026 ± 0.014 | + | + | | + | + | + | + |
| | Molybdenum | Mo | 0.133 ± 0.164 | + | + | + | + | + | | + |
| | Aluminum | Al | 0.092 ± 0.027 | + | + | + | + | + | + | + |
| | Barium | Ba | 0.31 ± 0.395 | | + | | | + | | + |
| | Bromine | Br | 0.041 ± 0.022 | + | + | + | + | + | + | + |
| | Chromium | Cr | 0.048 ± 0.053 | + | | + | | + | | + |
| | Polonium | Po | 0.007 ± 0.009 | + | + | | + | | | |
| | Rubidium | Rb | 0.02 ± 0.022 | | + | + | + | | + | + |
| | Rhenium | Re | 0.069 ± 0.042 | + | + | | + | + | + | + |
| | Selenium | Se | 0.003 ± 0.003 | | + | | + | + | | + |
| | Silicon | Si | 15.565 ± 1.82 | + | + | + | + | + | + | + |
| | Thorium | Th | 0.009 ± 0.012 | + | + | | | | + | |
| | Uranium | U | 0.006 ± 0.008 | + | + | | | | + | |
| | Zirconium | Zr | 0.007 ± 0.016 | | | | | + | | + |

"+" represent the presence of the element in the sample.

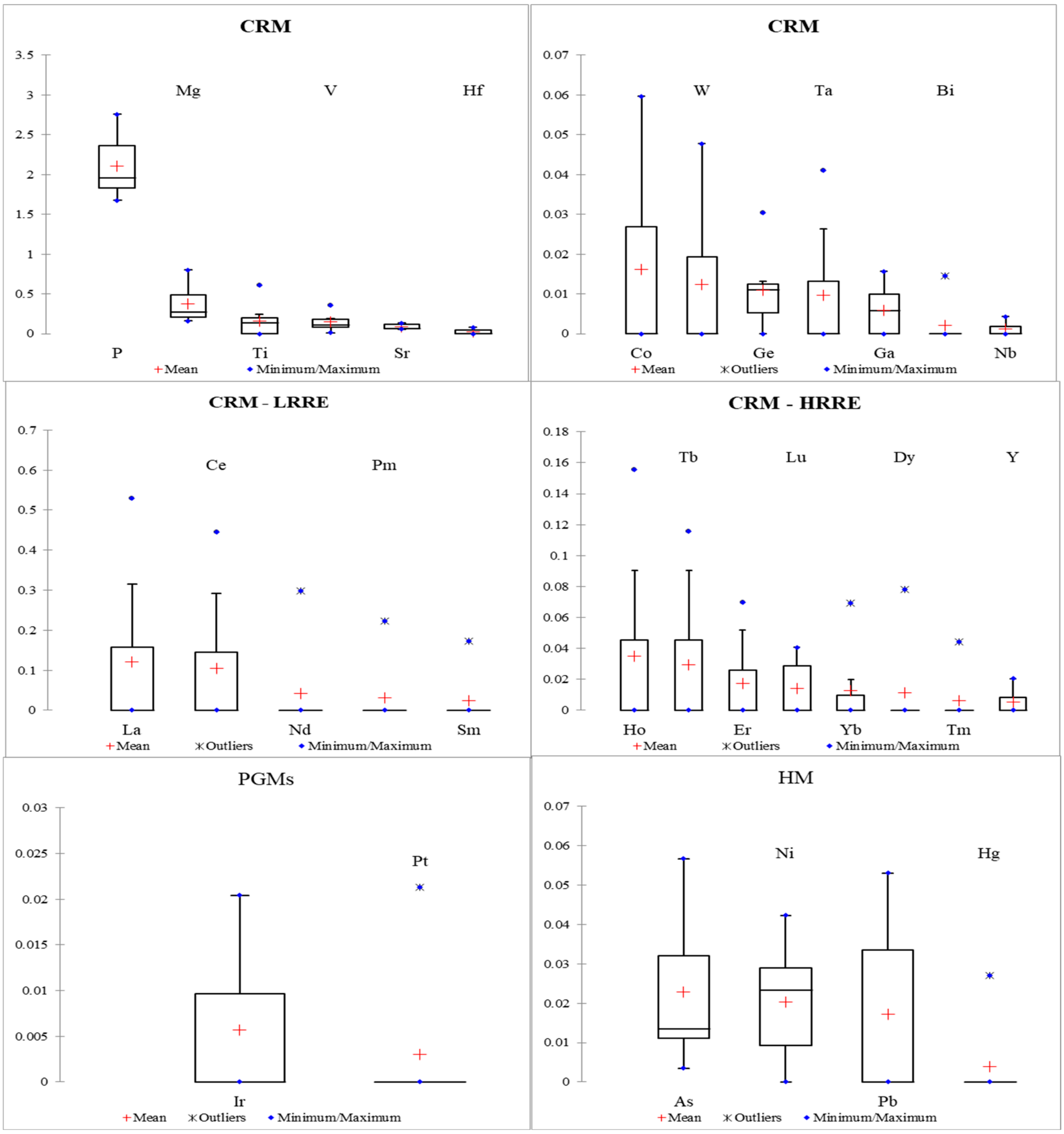

**Figure 2.** Boxplots (minimum, maximum, mean, and outliers) represent the critical raw material and heavy metal categories in *P. australis* from the studied sites. The CRMs follow the EU list, with other critical elements and separately Rare Earth Elements (REE) (with heavy and light REE) and Platinum Group Metals (PGMs). The elements from the box plots are presented in descending order of concentration (in mg kg$^{-1}$).

The element content of the *P. australis* ash showed through AHC a grouping of the studied areas related to the anthropogenic influence (Figure 4). Thus, the unmodified river areas outside urban areas, represented by stations 0 and 6, were differentiated into 2 clusters separate from the other stations. Additionally, the dendrogram that included the rest of the stations was also branched into different degrees of similarity as follows: Peri-urban stations 2 and 5 presented the highest similarity, secondary linked with stations 3, 4, and 1. The positioning of stations 1, 3, and 4 in the cluster emphasized the particular features of the selected areas. Thus, station 1 was the transition station between the peri-urban and rural areas, while stations 3 and 4 belong to the urban region of the river.

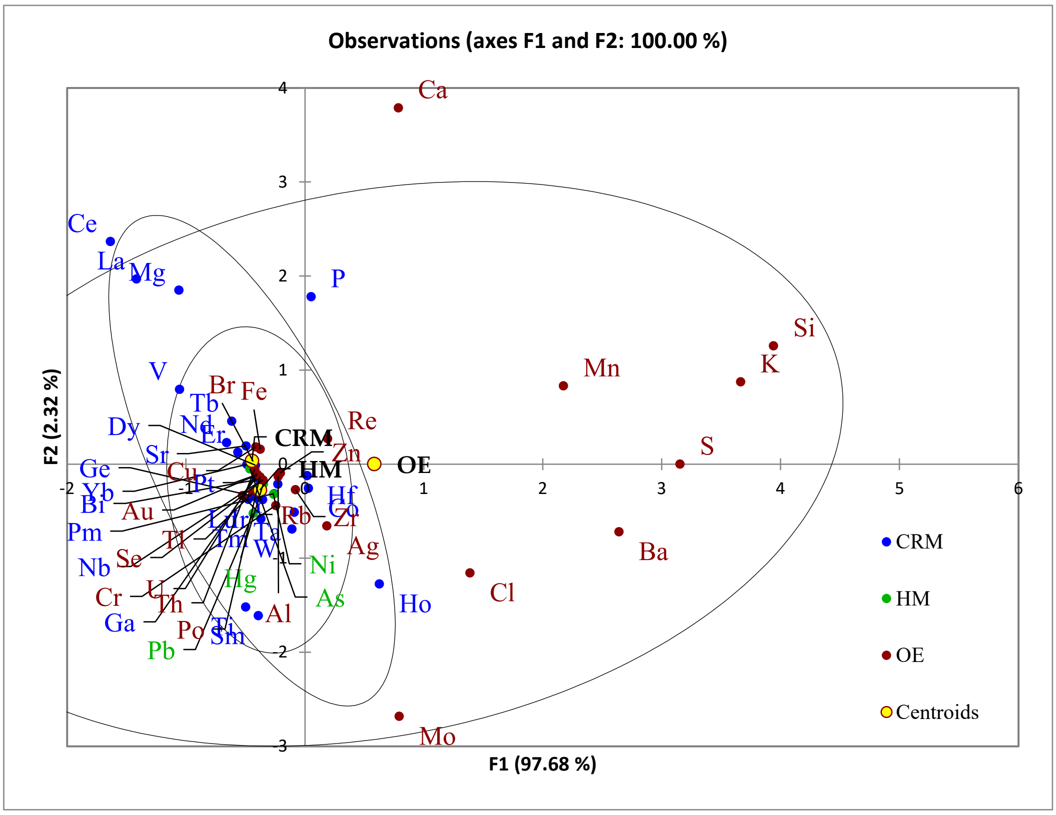

**Figure 3.** Discriminant analysis plot of element content in *P. australis* differentiated by the type and their participation as a weight in the *P. australis* ash.

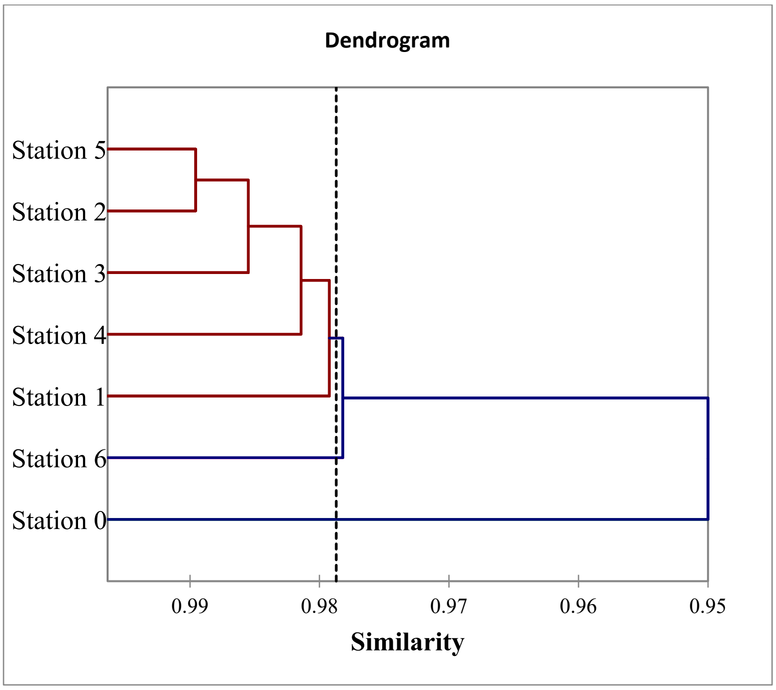

**Figure 4.** Agglomerative hierarchical clustering (AHC) based on element content by XRF analysis in *P. australis* from the studied sites.

## 4. Discussion

In the present times, great importance should be given to environmental education and the circular economy due to the constant increase of different types of waste in nature. The importance of element identification is underscored not only from a pollution point of view but also from the importance of some elements recognized as critical raw materials [25]. Furthermore, in such investigations, the X-ray fluorescence system proved to be a valuable tool to evaluate the compositional assessment in terms of research for the presence of potentially risky elements and other types of elements on the Colentina River (Table 1). Notably, among the elements identified in the study, urban lakes may induce different effects on aquatic ecosystems with potential harm, acute impacts, and long-term negative impacts. Regarding the presence of the representative elements of our study, most bibliographic sources highlight numerous sources of origin that are characteristic of anthropogenic activities. The expansion of the colonization of nature by human populations was achieved by transforming natural ecosystems into systems controlled or created by humans. It can be considered that the ecosphere has been transformed into hierarchical socio-ecological systems. The existing spatial structures in the city can be seen as elements of the support biotope for the biocoenosis existing here. Further, anthropization contributes to the modification of biotopes and biocenoses in urban areas, thus changing the quality and quantity of matter and energy flows between the city and nature. Several stress factors act on every level of biological organization, forcing organisms to adapt or die. Additionally, the biocenosis found in man-made systems and dependent on the energy subsidy from the natural environment, is vulnerable [26,27].

Further, among CRMs, bismuth-like metal is not toxic to the environment, and their compounds have very low solubility [28]. Similarly, hafnium (Hf) has no negative effects on plants [29], while tungsten (W) is not toxic to the environment [30]. The possible sources of titanium (Ti)—a critical raw material with toxic effects [31] Pollution may be represented by uncontrolled waste deposits (pigments in paint, sunscreen, and food coloring-E171) and maybe also introduced into the environment as nanoparticles via wastewater treatment plants [32]. Rosário et al., 2022 [31] identified that $TiO_2$NPs at a concentration between 0.75–75 mg/L have in vitro hepatotoxic and neurotoxic effects on human hepatoma and neuroblastoma cells. Vanadium (V)—a critical raw material with toxic effects—has numerous applications in the steel industry, air treatment, building materials, flooring, catalysts, colorants, plastic products, fluid property modulators, and manufacturing [33]. Recently, vanadium has attracted interest due to its effects on ecosystems, animal poisoning, and human diseases [34]. On the other hand, cerium (Ce) has different applications in industry (oxidizing/reducing plating agents), petroleum production (surface treating agents), electrical and electronic products, and environmental catalyst paints. Its accumulation has documented long-term adverse effects [35]; for this reason, it requires increased attention. In our case, cerium ($0.105 \pm 0.185$ mg $kg^{-1}$) was one of the five elements found after phosphorus, magnesium, titanium, and vanadium.

Although studies on the commercial benefits of CRMs recovery are very limited, recycling has a much lower impact than extraction from mines [36]. Cities urgently need proper waste management through policies and lawmaking, techno-economic mechanisms, a circular economy, and export/import control. Until now, although these elements are necessary for many industries, few studies have been conducted concerning their effects on the aquatic environment, plants, and humans.

The increasing usage of nanoparticles (especially those based on REE) for various industrial applications raised concerns about the impact on human and environmental health. Generally, there is literature available concerning the effects of different elements such as nitrate, chloride, and oxides as a whole, but extensive studies are required. At present, there is a relatively low amount of information about bioaccumulation and its effects on the environment (animals, plants, and human health). Some studies concerning REE toxicity were realized in the case of mineworkers [37]. More attention should be addressed to areas such as e-waste dumping sites and heavy-traffic urban areas [38].

The source of CRMs can also be different sectors of industry, such as renewable energy technology, glass making, metallurgy, etc. Despite the increased use in recent times, few data are available concerning the potential effects of these elements on plants [39].

The presence of a wide range of elements, including the series of lanthanides and actinides, can be supported by the pollution from anthropogenic sources that is brought into lakes by wind or by the flow of the water. The higher number of microorganisms identified in the studied lakes [40], together with the other natural factors, contribute to the degradation of these waste types that pollute the water. In this way, a significant number of chemical elements can be identified. The REEs are considered a group of nonessential and nonbeneficial chemical elements in plant life, but in excess they could imbalance ecosystems, causing severe environmental pollution [41]. In addition, the REEs were represented by elements with toxic effects and without risks to the environment. The plant assimilated some of them at an extremely low rate in the leaves. There are studies [42] that found correlations between REE from soil and essential plant nutrients, suggesting that REE are absorbed during Fe absorption. In this study, no correlation has been identified between these, which led us to the idea that the REE present in our samples can be determined by dust fall. A higher REE content was found on leaf surfaces compared to other plant parts due to dust [43].

According to Bonanno and Pavone 2015 [44] *P. australis* is an appropriate biomonitor for PGMs, a CRMs group with high interest. Its anthropic origin is mainly its use as a catalyst in fuels to reduce pollutant emissions [45]. In this group, two metals, platinum (Pt) and iridium (Ir), were found in our samples with an atmospheric origin. Pt was found in 1 station (Station 3) at a low concentration ($0.003 \pm 0.008$ mg kg$^{-1}$) and did not represent a health risk. No information concerning iridium effects on the environment was found. In our case, Ir ($0.005 \pm 0.009$ mg kg$^{-1}$) was found in Stations 1 and 2.

The silver and gold rare elements input into the environment became visible with modern technology (smartphones, digital cameras, computer parts, semiconductors). Silver is used in anticancer chemotherapy, antibiotics, and cosmetics [46] and could potentially harm the whole ecosystem [47]. Moreover, silver nanoparticles may come from textiles, medical products, domestic appliances, food containers, cosmetics, paints, and nano-functionalized plastics [48]. McGillicuddy et al., 2017 [48] mentioned in their article concerning silver nanoparticles in the environment that different aquatic life is influenced by these nanoparticles. The concentrations such as 190 µg/L or 180–1140 µg/L AgNP represent the $EC_{50}$ for *Pseudokirchneriella subcapitata*, depending on the nanoparticle coatings. Silver ($0.118 \pm 0.033$ mg kg$^{-1}$) was found in samples from all stations and gold ($0.006 \pm 0.01$ mg kg$^{-1}$) in 2 stations (stations 1 and 5). The noble metal concentrations in plants are lower under natural conditions: gold and platinum have low solubility, so plants do not normally accumulate them [49].

In most studies conducted on the subject, such as the identification of urban pollution pressures on aquatic ecosystems, the focus is mainly on the impact of heavy metals. However, the results of our study highlighted the presence of all airborne heavy metals (lead-Pb, arsenic-As, nickel-Ni, and mercury-Hg), in the samples, especially those associated with urban traffic. Further, while the analyses indicated low weights for these elements, arsenic showed higher concentrations compared to the other heavy metals. According to Wang 2009 [50], the heavy metal bioaccumulation in *P. australis* is influenced by substrate type, metal availability, and compound properties [46]. Arsenic has high toxicity for aquatic life [51] and may result from urban and industrial sources such as electroplating, metal smelting, the burning of fossil fuels, and chemical industry wastewater [52]. Nickel is used in different industries (biosensing, conductive coatings, data storage, lithium-ion batteries, magnetic fluids, fuel cells, optical technology, packaging, solar cells, and water purification [53], presenting direct and indirect toxicity [54]. Mercury has different uses, such as antiseptics, cell batteries, pigments, glass modifiers, fungicides, preservatives in cosmetics, and antifouling paints [55], and has acute and long-term effects on the aquatic environment [56]. The heavy metals' provenience is both natural (such as seepage and forest fires) and anthropogenic (industrial, agricultural, roadway, and automobile). In aquatic systems, heavy metals are not eliminated through natural processes but are accumulated by sediment, and the food web is known for its adverse effects [57,58]. The reed absorbs both the root system and the foliage surface [59]. The elements' complexity found in *P. australis* reflects both their availability from the environment and their structural component.

The results are in conformity with [14], and the heavy metal concentrations in *P. australis* strengthen its use as a widely accepted valuable bioindicator of pollution due to its absorbent capacity, although the accumulation depends on numerous factors [60].

Plants can absorb heavy metals due to their similarity in chemical structures with trace elements iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) [61]. The lower absorption of airborne heavy metals can be explained by the short vegetation period of *P. australis*, from March to July. In any case, as a result of its fast growth, the common reed is one of the most studied aquatic plants in the problem of water pollution [62,63].

Among the other elements, a high concentration of barium (Ba) was found. Chemicals originating from different sources (electronic devices, production of optical crown glass, reducing and oxidizing agents, and lubricating oil detergents are known to be harmful to aquatic organisms [64]. In our case, Ba was found in only 3 stations. A higher amount of Ba ($0.31 \pm 0.395$ mg kg$^{-1}$) was found in the periphery stations (1 and 6), which are ringed by agricultural lands. Our data are in accord with those of Malinowska & Novak [65], who found the highest Ba concentration in herbs from the sampling points surrounded by arable fields. With a lot of applications (electrical and electronic products, paints and coatings, water treatment products, air emission control, and raw material intermediates), sulfur (S) has toxic and long-lasting effects [66]. Moreover, elements such as macronutrients (N, P, K, Ca, Cl, Mg, and S) and micronutrients (Zn, B, Cu, Fe, Mn, and Mo) are indispensable for plant development. The nutrients, together with other elements such as Co, Mo, Ni, and Zn, perform important functions in plant development such as redox reactions or are integral parts of enzymes [66].

In addition, while there are laws for environmental protection limits for heavy metals, pesticides, etc., the data from the literature emphasizes their presence in nature (accidental or not) and their effects on the environment. For this reason, it is acutely important to have fast methods to identify pollution. As a result of the plot resulting from DA, a significant input of elements with anthropogenic origin was highlighted; these were represented by heavy metals and part of the elements in the CRMs category (Figure 4). The *P. australis* distribution on the studied river was determined by the environmental conditions and the administrative cleaning activities of some lakes. The results of the AHC analysis (Figure 4) show, through the composition of the elements, the influences of regional anthropogenic activities [67], which refer to agriculture, rainwater, road traffic, and nearby industrial units and households. The similarity cluster of the lakes (stations 1, 2, 3, 4, and 5) could be explained by 13 elements (Au, Ce, Ga, Ho, Ir, Nb, Pm, Pt, Sm, Ta, Tl, Tm, and W) present only in these stations, which add 19 common elements (present in at least 6 stations) (Table 1). Further, their association could be determined by some rare elements. For example, lutetium (Lu) and thallium (Tl) were limited and present in 2 stations (stations 2 and 5) far from each other; promethium (Pm) was only in station 1, neodymium (Nd) was only in station 6, and bismuth (Bi) and dysprosium (Dy) were found only in station 0 (Table 1). All elements derive from human activity, even pollution with historical origins such as pesticides and pharmaceuticals [68,69]. The locations of stations 0 and 6 on the river course also justify their position in the cluster. Station 0 is subject to regional agricultural influences, while station 6 receives water from upstream urban ecosystems and adjacent agricultural areas. However, the cluster highlighted differences between the studied areas, thus signaling different sources of contamination along the river; however, the low concentrations of most elements make these variations not significant. According to Müller et al. [49], there are also other factors, such as buildings and infrastructure, construction, roof surfaces, fences, railings, etc., which contribute, in addition to known factors, to urban pollution. The pathways of accumulation in aquatic ecosystems are precipitation and atmospheric deposition. Thus, they can be considered results of the existence of common sources of origin, which are reflected in the bioaccumulation processes.

## 5. Conclusions

The results of the study indicate the presence of human influences on the course of the Colentina River. The presence of different elements (such as CRMs or heavy metals) varied depending on the regional influence. Additionally, the compositional complexity of the urban ecosystems makes the studies challenging but important in raising awareness of the risks to which we are exposed in modern society. Further, the weight of the elements identified in our study may represent a moderate risk, typical of urban ecosystems, but with a high potential for resilience if local management is improved. Useful measures consist of limiting the sources of diffuse and point pollution. However, more frequent dredging, maintenance, and water refreshment work by controlling the lock system on the Colentina River would improve the existing conditions. In the future, we intend to monitor the river, analyze the bulk sediments, and create a pollution risk map.

**Author Contributions:** Conceptualization, R.D.C., L.I.F. and M.M.; methodology, R.D.C., L.I.F., A.P. and M.M.; software, R.C.; validation, M.E.; formal analysis, A.P.; investigation, R.D.C., L.I.F. and R.A.M.; writing—original draft preparation, R.D.C. and L.I.F.; writing—review and editing, M.M., M.E. and R.C.; project administration, M.M. and M.E.; funding acquisition, M.E. All authors have read and agreed to the published version of the manuscript. R.D.C., L.I.F. and A.P. have equal contributions.

**Funding:** This research was funded by the Institute of Biology Bucharest of Romanian Academy, grants numbers RO1567-IBB02/2021, RO1567-IBB05/2021, and RO1567-IBB08/2021, and S.C. MEDACRIL S.R.L. Medias, grant number AMBAL-INOV, My SMIS code: 120994.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The authors thank Gavrilidis A.A. for delivering the map.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study, in the collection, analysis, or interpretation of data, in the writing of the manuscript, or in the decision to publish the results.

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