Scientific Papers. Series E. Land Reclamation, Earth Observation & Surveying, Environmental Engineering. Vol. XV, 2026
Print ISSN 2285-6064, CD-ROM ISSN 2285-6072, Online ISSN 2393-5138, ISSN-L 2285-6064

XRF-BASED ASSESSMENT OF ELEMENT ACCUMULATION IN *PHRAGMITES AUSTRALIS* ACROSS FRESHWATER, URBAN, AND SALINE AQUATIC ECOSYSTEMS: IMPLICATIONS FOR NATURAL FILTRATION AND ENVIRONMENTAL RISK

Mirela Mădălina MOLDOVEANU[1], Larisa Isabela FLORESCU[1], Raluca Alexandra MIHAI[2], Cristian BANCIU[1], Maria Iasmina MOZA[3, 4], Doru Simon DOBRE[1], Cristina Alina DUMITRACHE[1, 5], Rodica Daniela CATANĂ[1]

[1]Institute of Biology Bucharest of Romanian Academy, 296 Splaiul Independentei, District 6, Bucharest, Romania
[2]CIAM, Department of Life Science and Agriculture, Universidad de Las Fuerzas Armadas-ESPE, Av. General Ruminahui S/N y, 171103 Sangolqui, Ecuador
[3]University of Bucharest, Faculty of Biology, Department of Botany and Microbiology, 91-95 Splaiul Independentei, District 5, Bucharest, Romania
[4]Moza Foundation, 1 Cetatea Histria, Bucharest, Romania
[5]School of Advanced Studies of the Romanian Academy (SCOSAAR), 010071, Bucharest, Romania

Corresponding author email: larisa.florescu@ibiol.ro

Abstract

Our study uses X-ray fluorescence spectroscopy to assess element accumulation in Phragmites australis across three distinct aquatic environments. We identified spatial patterns reflecting both the natural background and varying levels of human influence. Natural freshwater exhibited moderate concentrations of geogenic elements, including calcium (Ca), strontium (Sr), barium (Ba), manganese (Mn), and titanium (Ti). In contrast, urban freshwater showed higher levels of iron (Fe), aluminium (Al), copper (Cu), zinc (Zn), and lead (Pb). This indicates an anthropogenic signature associated with runoff, wastewater, and urban infrastructure. Saline lakes exhibited distinct elemental profiles, characterised by elevated levels of sodium (Na), potassium (K), calcium (Ca), and chloride (Cl). These patterns suggest mineralisation processes and physiological adjustments to cope with salinity stress. Rare elements (astatine (At), found in deltaic and urban locations) indicate localised geochemical traits. The accumulation patterns across ecosystems highlight the dual ecological role of the reed. It acts as a natural filtration system, and it can also serve as a potential vector for transferring elements within food webs. These findings support the use of Phragmites as a bioindicator for assessing environmental quality.

Key words*: aquatic ecosystems, element accumulation, environmental risk, natural filtration, Phragmites australis.*

INTRODUCTION

Aquatic ecosystems are subject to increasing geochemical and anthropogenic pressures from industrial activities, agriculture, urbanisation, and climate change. In these systems, geochemical processes are dynamic, and thus common elements and potentially toxic metals are mobilised, transported, and transformed in water bodies through complex interactions. Under these conditions, emergent vegetation acts simultaneously as a biogeochemical interface, a biological filter, and a bioindicator of environmental conditions. The species *Phragmites australis* (Cav.) Trin. ex Steud, it is extremely widespread and adaptable to different conditions, with a remarkable capacity to colonise diverse habitats, from freshwater ecosystems to hypersaline waterbodies or urban systems. The species is characterised by high biomass production and stress tolerance, which is why it is frequently used in phytoremediation and pollution monitoring studies (Chapligin et al., 2022). In addition, its ability to accumulate elements from sediments, water, and atmospheric deposition makes it a valuable bioindicator of metal contamination and local geochemical processes (Weis & Weis, 2004; Chitimus et al., 2023). The sediment composition, water chemistry, salinity,

hydrological dynamics, and anthropogenic pressures influence the distribution and uptake of elements in aquatic biota. For example, lithogenic elements generally reflect the natural geochemical background and sedimentary features and transport, thus indicating aspects of mineral fractions and detrital processes (Taylor & McLennan, 1995; Cullers, 2002). In saline and hypersaline environments, salinity plays a major control factor, influencing the mobility and bioavailability of elements through complex geochemical processes such as chloride complexation, flocculation, and authigenic precipitation. These processes can significantly modify the distribution of elements, affecting their availability to aquatic organisms and emergent vegetation (O'Day et al., 2004; Warren, 2006; Acosta et al., 2023).

A major focus is on potentially toxic elements such as As, Pb, Cu, Zn, and Ni, which are frequently associated with industrial activities, road traffic, and atmospheric deposition (Pacyna & Pacyna, 2001; Thorpe & Harrison, 2008; Charlesworth et al., 2011). Recently, there has been a particular interest in rare earth elements (REE), which are increasingly used as geochemical tracers due to their conservative behaviour and sensitivity to sedimentary fractionation and transport processes (Piper & Bau, 2013; Song et al., 2023; Hatje et al., 2024). Studying the accumulation of REE in plant biomass can provide valuable information about sedimentary sources, redox conditions and biological uptake mechanisms. In the context of increasing anthropogenic pressure on wetlands, assessing plant elemental uptake offers an integrative approach to understanding biogeochemical processes. X-ray fluorescence (XRF) analysis offers a rapid and robust method for the simultaneous determination of a wide spectrum of elements in biological and sedimentary material (Jenkins, 1999; Mondal et al., 2021).

The aim of the study is to evaluate elemental accumulation in *Phragmites australis* from deltaic, urban, and saline aquatic ecosystems using XRF analysis, and to determine the role of the species as a geochemical bioindicator and natural filter of contaminants. The objectives are: the determination of the elemental composition, the comparison of geochemical traits between *deltaic*, *saline* and urban ecosystems, the identification of potential sources of elements and the evaluation of the influence of ecosystem conditions on the bioavailability of elements.

Despite the extensive use of *Phragmites australis* as a bioindicator, comparative assessments across freshwater, urban, and saline ecosystems remain limited. Existing studies rarely integrate geogenic, anthropogenic, and rare earth element signatures into a unified ecological interpretation. This study addresses this gap by providing a multi-environmental evaluation of elemental accumulation patterns using XRF.

MATERIALS AND METHODS

Study site. The sampling of *Phragmites australis* specimens was carried out, including both aboveground and belowground biomass from each sampling point from ecotonal areas associated with different types of aquatic waterbodies as follows (Figure 1):

• Brackish/*saline* ecosystems: Braila Salt Lake, Techirghiol Lake and Musura Bay.

• *Urban* freshwater ecosystems: Fundeni and Cernica lakes.

• Danube Delta freshwater ecosystems: Eracle Canal, Sulina Branch and Rădăcinos, La Amiază, Miazăzi, Matița and Bogdaposte lakes.

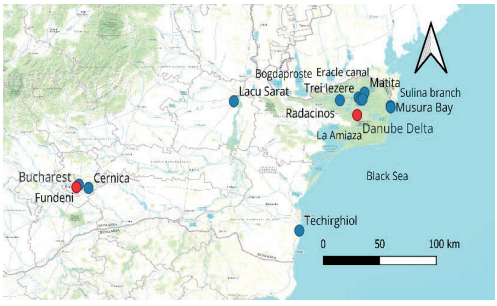


Figure 1. The map of the sampling stations (the red dots-Danube Delta and Bucharest, blue dots - sampling points) - (QGIS 3.40.15- an open-source Geographic Information System)

At each site, three independent *Phragmites australis* specimens were collected to ensure spatial representativeness. Both aboveground and belowground tissues were sampled from individuals located at least 5 meters apart to avoid clonal redundancy. All samples were

collected during the same season to minimize phenological variability.

Laboratory analysis. Leaves and roots were separated and prepared for laboratory analysis. The plant material was dried for 2 hours at 60°C, then mechanically ground with a porcelain mortar and pestle. 20 g were taken from each sample, which were subsequently subjected to a calcination process for 2 hours at 550°C in a muffle furnace (Nabertherm LE 6/11/B150). The obtained ash was analysed for elemental composition using a wavelength-dispersive X-ray fluorescence spectrometer (Rigaku ZSX100e, Supermini model). The equipment allows the identification of elements at concentrations of 0.1-100%. For analysis, 1 g of ash was introduced into 30 mm-diameter sample cells, sealed on both sides with 6 μm polypropylene foil, and fixed with a Snap-On ring. The method principle consists of irradiating the sample with X-rays and recording the characteristic reflection angle (θ) for each element. The instrument software converts the signal intensity into mass percentages of elementary oxides (Jenkins, 1999). The percentage values obtained were transformed into absolute concentrations (mg kg^{-1} dry weight) (Mondal et al., 2021). The XRF method may underestimate volatile elements such as Hg, Se, and S due to partial loss during calcination at 550°C. Additionally, elements present near the detection limit (0.1%) may exhibit higher analytical uncertainty. These limitations were considered when interpreting trace and rare element concentrations.

The detected elements were grouped into functional categories based on their predominant ecological role and environmental origin. Classification criteria included geogenic background versus anthropogenic contribution, biological relevance, and toxicity. Thus, elements were assigned to (1) geogenic/macronutrients, (2) anthropogenic and potentially ecotoxic metals, (3) rare earth elements (REE), and elements identified in low/trace concentrations.

Data processing. Principal Component Analysis (PCA) was used to explore relationships among the identified elements and to reduce the dataset's dimensionality while preserving most of the total variation (Legendre & Legendre, 2012). Agglomerative Hierarchical Clustering (AHC) was applied to identify similar groupings between elements based on the analysed characteristics (Kassambara, 2017). Analysis of Similarities (ANOSIM) was used to test differences in elemental composition among ecosystem types (Clarke, 1993). The data were transformed by log(n+1). The statistical processing was performed using the XLSTAT add-in (version 2014) and PAST 4.16c (Hammer et al., 2001).

RESULTS AND DISCUSSIONS

Elemental composition of Phragmites australis across ecosystem types.

The results are presented according to the three functional groups of elements: geogenic/macronutrients, anthropogenic metals, and rare/trace elements. Differences among deltaic, saline, and urban ecosystems are highlighted to identify the dominant environmental drivers shaping elemental accumulation in *Phragmites australis*. Analysis of the elemental composition of *Phragmites australis* samples revealed differences in element content across the ecosystems investigated. 58 elements were identified, which varied spatially as follows: 55 *deltaic* > 48 *urban* > 45 *saline* ecosystems. The *urban* environment showed enrichment in metals of anthropogenic origin; the natural *deltaic* ecosystems were dominated by elements indicative of lithogenic input; and the *saline* environments were characterised by elements influenced by the geochemistry of mineralised waters (Table 1, Table 2, and Table 3).

The *deltaic* environment was characterised by elevated concentrations of Fe, Rb, Zr, and elements from the REE category (Table 1, Table 2), indicating the influence of fluvially transported detrital matter and fine sediments rich in mineral fractions. Thus, the composition of the reed in this sector mainly reflected the natural geochemical background and less anthropogenic pressure. In addition, the high variability in Fe, Zn, and Cr may indicate heterogeneous sources and variable conditions for mobilisation and bioaccumulation.

In contrast, in the *saline* lakes, higher concentrations of Hg, Ba, Sr and Mo were recorded (Table 1, Table 3), an association that

may suggest specificities in the mobilisation of elements under conditions of high salinity and a specific redox potential, reflecting the hydrogeochemical characteristics of this type of habitat.

Table 1. The geogenic group elemental concentrations (mg/kg DW) in *Phragmites australis* across *deltaic*, *saline*, and *urban* ecosystems

	Deltaic	***Saline***	***Urban***
Al	0.001	0.008	N/A
Ba	0.135±0.089	0.216±0.124	0.206±0.091
Br	0.009±0.01	0.018±0.014	0.049
Ca	0.016±0.012	0.007±0.004	0.018±0.012
Cl	0.006±0.006	0.004±0.003	0.003
Fe	0.182±0.15	0.155±0.144	0.054±0.067
I	0.087	0.031	
K	0.03±0.021	0.021±0.013	0.02±0.008
Mo	0.005	0.026±0.036	0.017±0.007
P	0.01±0.005	0.03±0.021	0.035±0.008
Rb	0.027±0.03	0.004±0.001	0.007±0.003
S	N/A	0.002	N/A
Se	0.01±0.009	0.011±0.005	0.019±0.016
Si	0.009±0.008	0.009±0.008	0.007±0.007
Sr	0.011±0.003	0.018±0.014	0.012±0.004
Th	0.014		0.031±0.012
Ti	0.047±0.026	0.056±0.043	0.094±0.066
U	0.011±0.002	N/A	0.014±0.003
Zr	0.034±0	N/A	N/A

Table 2. The REE and trace groups elemental concentrations (mg/kg DW) in *Phragmites australis* across *deltaic*, *saline*, and *urban* ecosystems (REE - Ce-Y, trace elements – Ag-W)

	Deltaic	***Saline***	***Urban***
Ce	0.129±0.09	0.121±0.04	0.128±0.02
Dy	0.042±0.021	0.052±0.045	0.095±0.048
Er		0.03±0.015	0.039±0.008
Eu	0.014	0.063±0.082	0.007
Gd	0.09	0.12±0.042	0.082±0.019
Ho	0.055±0.034	0.059±0.029	0.08±0.01
La	0.17±0.214	0.18±0.096	0.178±0.048
Lu	0.05±0.027	0.092	
Nd	0.186	0.087±0.054	0.092±0.041
Pr	0.098±0.083	0.195	0.183±0.026
Sm	0.031	0.067±0.056	0.082±0.038
Tb	0.041±0.036	0.045±0.032	0.083±0.003
Tm	0.008	0.032±0.038	
Y	0.012±0.012		0.054±0.064
Ag	0.065±0.025	0.077±0.043	0.103±0.079
Au	0.025±0.003	0.041±0.032	0.063±0.02
Bi			0.055±0.03
Ga	0.006±0.002	0.022	0.018
Ge	0.036±0.026	0.025±0.018	0.044±0.003
Hf	0.065±0.045	0.076±0.003	0.139
Ir		0.039±0.006	
Nb	0.009±0.007	0.007±0.003	0.013±0.009
Pt	0.042		0.022
Re	0.054±0.015	0.05±0.027	0.054±0.027
Ta		0.007	
W	0.04±0.04	0.029	0.029

Elements indicating anthropogenic activity showed an obvious enrichment in the *urban* environment, with higher values recorded for As, Pb, Mn, and Tl (Table 3), as well as Br, suggesting the influence of pollution sources associated with traffic, industrial activities, and atmospheric deposition (Wei & Yang, 2010).

Table 3. The anthropogenic group elemental concentrations (mg/kg DW) in *Phragmites australis* across *deltaic*, *saline*, and *urban* ecosystems

	Deltaic	***Saline***	***Urban***
As	0.048±0.038	0.043±0.023	0.069±0.023
Co	0.004±0.001	0.019±0.005	0.018±0.006
Cr	0.074±0.078	0.035	0.073±0.097
Cu	0.015±0.012	0.003	0.01±0.007
Hg	0.025±0.009	0.07±0.041	0.038
Mn	0.049±0.029	0.045±0.028	0.093±0.039
Ni	0.025±0.019	0.003	0.019
Pb	0.081	0.052±0.037	0.083
Sb	0.068	0.016	
Te	0.079	0.027	
Tl	0.029	0.029±0.027	0.049
V	0.046±0.014	0.053±0.05	0.035±0.017
Zn	0.058±0.072	0.02±0.017	0.017±0.012

Recent studies have shown that Phragmites australis can effectively bioaccumulate Fe, Mn, Cd, Cr, Ni and Pb, with most metals being retained in belowground tissues, highlighting its phytostabilization potential (Samadi et al., 2024). This distribution supports the reed's ability to retain and integrate metal contaminants from the water column and

sediments, functioning as a biological filter of *urban* pollution.

ANOSIM analysis indicated a statistically significant difference between ecosystems (R = 0.0786, p = 0.0179), with distinct elemental content between at least two of the analysed habitat types. Although the analysis highlights a reduced separation between groups, paired tests indicate that the significant difference is primarily driven by the contrast between *deltaic* and *urban* areas (p = 0.0015). There were no significant differences between *deltaic* and *saline* (p = 0.37) or between *saline* and *urban* (p = 0.29).

Regarding the weight of the groups in the sample (Figure 2), the results showed that geogenic elements (Fe, Ba, Mn, Ti, Ca, K) were dominant, reflecting their structural role and their availability in sediments. The identified elements also varied slightly depending on the habitats evaluated, such as in *deltaic* (Fe>Ba>Mn>Ti), in *saline* (Fe>Ba>Ti>Mn), but in *urban* (Ba>Mn>Ti>Fe) (Table 1, Table 2, Table 3) ecosystems. This predominance reflects the availability of elements, which varies across ecosystems and with plant assimilation under different environmental conditions. In contrast, elements of anthropogenic origin (As, Cr, Zn, Cu, Ni, Pb, Sb) were present at lower levels, but their clear presence indicated external contributions from human activities. This was observed through the dominance of these elements, which varied slightly depending on the type of ecosystem, in the delta (As>Cr>Zn>V), while in the *saline* (As>V>Hg>Pb) and *urban* ecosystems (As>Cr>Pb>V) (Table 1, Table 2, Table 3). N/A values in the tables indicate concentrations below the detection limit of the XRF instrument or signals that could not be reliably quantified due to matrix interferences.

The share of elements with a very low content (trace) as well as of rare earth elements (REE - La, Ce, Nd, Pr or Dy) (Figure 2), may reflect local lithological particularities, but the ability of the reed to accumulate selectively. The REE distribution revealed a differentiated pattern of fractionation across environments (Table 2), suggesting variations in sedimentary sources, redox conditions, and biological absorption mechanisms, providing an ecological indicator (Song et al., 2023). This selective accumulation is essential, as REEs form a chemical group that can facilitate understanding of aquatic or terrestrial conditions, whether natural or anthropogenic (Hatje et al., 2024).

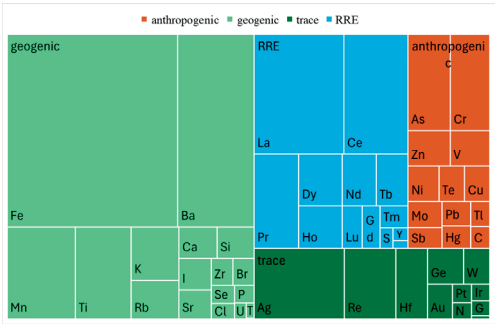


Figure 2. Elemental composition of *Phragmites australis* samples

PCA based on elements indicative of anthropogenic pollution (Figure 3) revealed a close relationship between the *deltaic* and *urban* environments, suggesting common anthropogenic influences or the transport of contaminants into the *deltaic* system, while the *saline* ecosystems remained distinct due to the dominant natural geochemical control. PCA analysis of elements related to anthropogenic sources revealed a cumulative weight of approximately 94% across the two axes. These elemental features confirm the major influence of anthropogenic sources on the reed's elemental composition, especially through contributions from heavy metals from industrial activities, road traffic, and combustion processes. PC1 groups elements of mixed origin, associated with traffic and fuels (Sb, Cu, Ni), fossil-fuel combustion (V, Mo), and industrial activities (Cr, Co, Tl, Te).

The biplot also shows a strong negative association for Sb, Te, Cu, Ni, Co, Mo, and Tl, elements that are frequently correlated with industrial emissions, wear of metallic materials, road traffic, and fossil fuel combustion. This association indicates anthropogenic inputs through atmospheric deposition, industrial effluents or fluvial transport of contaminated particles.

In contrast, As presents a high positive loading, suggesting a distinct source or a different biogeochemical behaviour in the analysed

system. The elements Cr and V, with moderate positive loadings, indicate additional influences related to metallurgical processes and liquid fuels. Hg, V, and Pb were associated with PC2, suggesting a secondary factor driven by atmospheric deposition and fuel combustion. Overall, the three ecosystems exhibited distinct geochemical fingerprints. Deltaic sites reflected lithogenic inputs, saline sites showed signatures of mineralized waters, and urban sites displayed clear anthropogenic enrichment. These patterns confirm that *Phragmites australis* integrates both natural and human-derived geochemical signals.

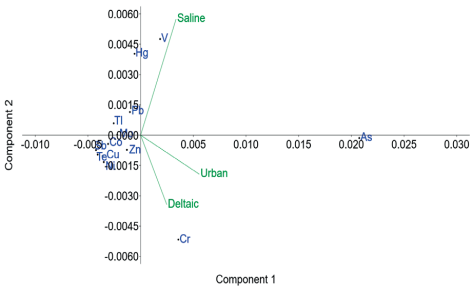


Figure 3. PCA - with elements indicating anthropogenic activities - in the three types of ecosystems

For elements of natural origin (Figure 4), PCA indicates a clear dominance of the first principal component, which explains 90.41% of the variance, while PC2 contributes 9.16%. The elemental composition is dominantly influenced by the geological substrate, *deltaic* sediments and natural processes of plant assimilation. This distribution suggests strong control by a major geochemical factor, highlighted by PC1, which separates lithophile elements from those associated with heavy minerals derived from sediments or deposited on leaves. Fe, Ba, Mn, and Ti, elements characteristic of oxides and detrital minerals, were grouped opposite Al, Si, K, Ca, Zr, Th, and U, indicating their association with the aluminosilicate fraction and resistant minerals in sediments. This component reflects lithogenic input, determined by alluvial transport, basin erosion, and sedimentary deposition. PC2 captures secondary variations in the mobility of elements (Ba, Mn, Ti) that reflect hydro-geochemical conditions, redox, salinity, and sediment availability.

The PCA analysis of rare and trace elements (Figure 5) shows that PC1 explains 87.46% of the variance, followed by PC2 (8.89%), indicating a clearly defined structure. It separates *urban* from natural environments through anthropogenic inputs with low trace-element content.

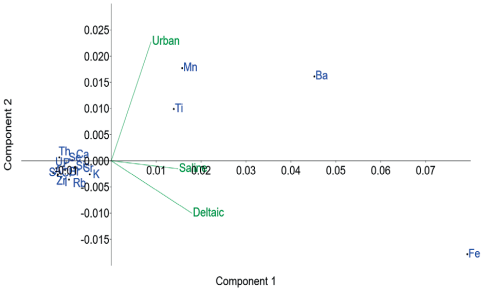


Figure 4. PCA - with elements indicating natural origin - in the three types of ecosystems

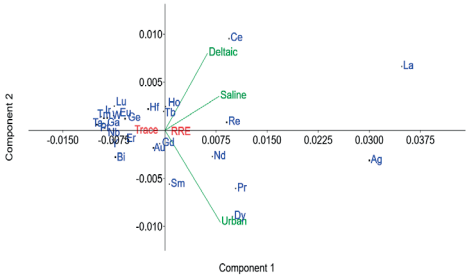


Figure 5. PCA - with elements indicating REE and Trace - rare elements

The *deltaic* ecosystems were subject to natural processes of uptake from sediment, slightly differently from *saline* ecosystems, indicating the influence of salinity, mineral characteristics, and plant availability. The distribution of REE and trace elements reflected the interactions among geogenic inputs (mineralogy, sediment composition), the ecological dynamics of the analysed ecosystems, and anthropogenic influences. PC1 highlighted a gradient in element separation of La, Ce, Pr, and Nd (light rare earth elements-LREE), with elements predominantly associated with stable mineral fractions of lithogenic origin and platinum-group metals

(Ta, Nb, W, Pt, Ir). This distribution reflects the geochemical fractionation and mineralogical control of the sediments. In contrast, PC2 highlights the differentiation of ecosystems: the *deltaic* and *saline* environments showed positive loadings, whereas the *urban* ecosystem exhibits a strong negative loading, suggesting anthropogenic influences on the distribution of trace elements. The detection of rare elements such as At, Ir, and Ta likely reflects localized mineralogical features or the presence of fine sediment fractions adhering to plant tissues. Their low concentrations suggest geogenic origins rather than biological uptake.

The PCA identified the major geochemical gradients, separating *deltaic*, *saline*, and *urban* systems based on dominant elemental features. In addition, AHC dendrograms allow the identification of element associations reflecting complex sediment/water processes. Hierarchical analysis based on Agglomerative hierarchical clustering (AHC) of the elements identified in *deltaic* ecosystems, highlighted a geochemical organisation structured into four major element associations, suggesting mineralogical mechanisms and other physical, chemical and biological processes taking place in the sediments (Figure 6). The first cluster (blue) groups predominantly lithogenic elements, associated with heavy minerals, including light and middle lanthanides (La, Eu, Gd, Tb), actinides (Th, U), high-field elements (Zr, Ta), as well as noble metals (Pt, Ir, Au), along with Sr and Ba. Their association indicates a common source related to the transport of fine particles, possibly enriched by anthropogenic input and distinct from the natural lithogenic background, a feature frequently reported in fluvial and *deltaic* sediments (Taylor & McLennan, 1995; Cullers, 2002). A second cluster (brown), much smaller, is dominated by Zn, Ag, and W, with Ti and Ce added. Zn and Ag are known as markers of metallurgical activities and fluvial transport of contaminated particles, and their association with W has been reported in sediments affected by industrial discharges (Förstner & Wittmann, 2012). The third group (pink) brings together elements characteristic of the clay fraction and oxides such as K, Rb, Si, Mn, V and Cr, together with potentially toxic metals (Cu, Pb, Hg) and part of the REE (Nd, Pr, Sm, Y). This association reflects the role of fine phases as a geochemical support for adsorbed metals. The last group (green), defined by Ca and Fe, correlated with P, As, Se, and Tl, indicating a carbonate- and redox-sensitive association characteristic of reactive sediments from environments rich in organic matter. This covariability reflects natural ecological processes of element fixation and release in iron oxides, controlled by oxidation-reduction cycles and interactions with carbonate and organic matter (Belzile & Tessier, 1990).

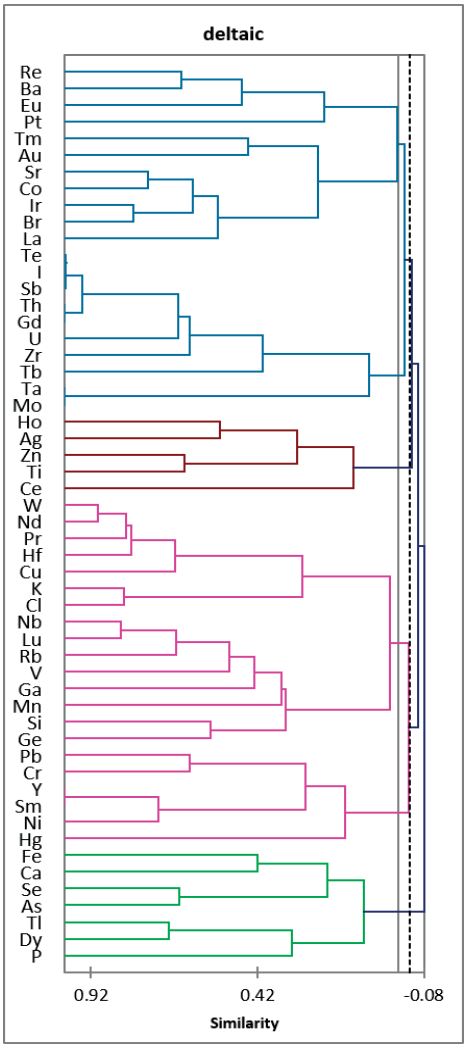


Figure 6. Agglomerative hierarchical clustering (AHC) of elements identified in *deltaic* ecosystems

In *saline* environments, AHC analysis revealed a more compact organisation into three distinct clusters, reflecting the typical chemistry of these ecosystems (Figure 7).

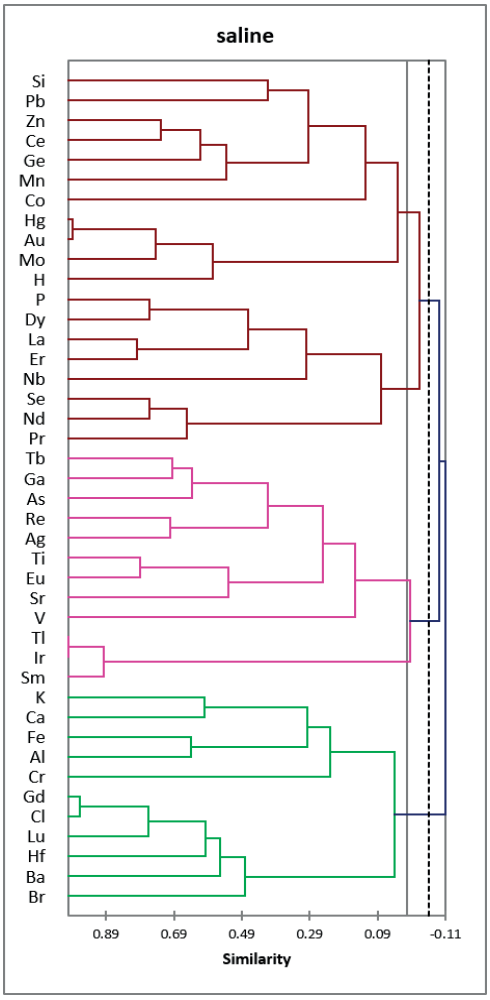


Figure 7. Agglomerative hierarchical clustering (AHC) of elements identified in *saline* ecosystems

A first cluster (brown) groups Si together with Pb, Zn, Ge, Mn, Co, Hg and Mo, indicating an association between the detrital fraction and contaminated metals. The cluster composition suggests that pollutants are transported and retained on mineral particles. Such associations have been reported in *saline* environments where salinity-induced flocculation favours metal retention (Acosta et al., 2023). The second cluster (pink) comprises metalloids and redox-sensitive metals, such as As and Tl, correlated with Sr, V, Ag and neighbouring some of the REE (La, Nd, Pr, Tb, Eu). This association indicates increased mobility in the dissolved phase, followed by re-fixation. Chloride complexation and redox variations enhance the mobility of elements, followed by their re-fixation via adsorption or co-precipitation (O'Day et al., 2004), thereby influencing the availability of nutrients and metals to microbial and benthic communities. Their correlation with Sr and REE indicates the involvement of authigenic phases, a common natural process in lakes and *saline* environments, reflecting active interactions between sediment chemistry and local ecological dynamics (Jones et al., 2005). The third cluster (green) is characterised by evaporitic and carbonate elements: Cl and Br correlated with Ca, Ba, K, Fe, and Al, suggesting authigenic precipitation under conditions of intense evaporation, a process that shapes sedimentary structure and influences the microhabitats of organisms adapted to *saline* environments. Cl/Br ratios are widely used to distinguish marine from continental sources, and the Ba-Ca correlation indicates barite and carbonate precipitation under conditions of intense evaporation (Holland et al., 1987). Therefore, *saline* ecosystem markers reflect three major processes as the input of potentially contaminating fine particles, the mobilisation of metals in *saline* waters, and authigenic precipitation of salts, a pattern commonly found in many *hypersaline* systems (Warren, 2006).

The *urban* dendrogram highlights a structure organised into three distinct clusters (Figure 8). A first major cluster (brown) brings together Zn, Cu, Ni, Mn, Pt, Hg, P, Ba and Sr, indicating a strong anthropogenic association. The high correlations among these elements suggest a common source related to traffic and industrial activities.

The second cluster (pink) was defined by Fe and Cr, and correlated with Se, Ag, and Si, indicating reactive oxide phases associated with *urban* fine particles.

The third, much broader cluster (green), included K, Rb, Ca, Ti, Nb, Th, As, V, Tl, Br and numerous REE (Pr, Gd, Tb, Sm, Dy, Y), suggesting a mixed origin related to *urban* dust and construction materials.

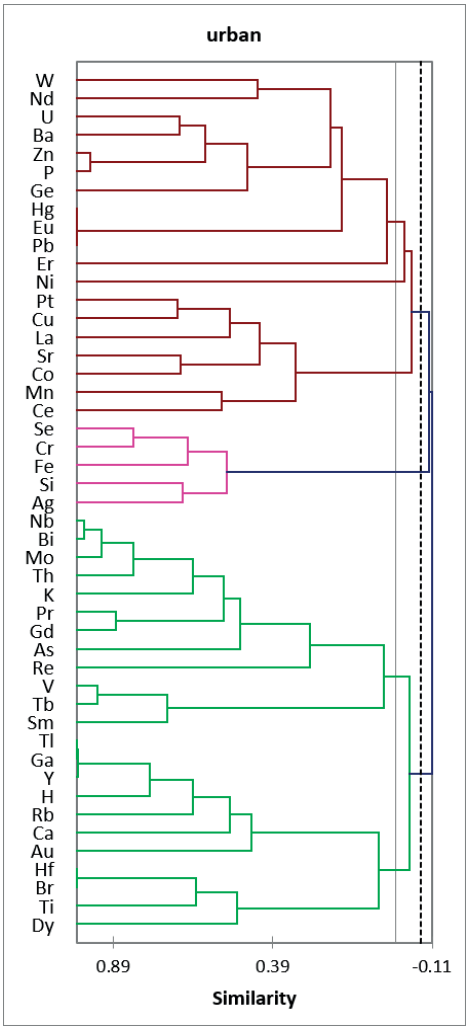


Figure 8. Agglomerative hierarchical clustering (AHC) of elements identified in *urban* ecosystems

The *urban* geochemical signature was dominated by multiple anthropogenic sources. The Zn–Cu–Ni association is considered a robust indicator of tire wear and brake systems, while Pt is an established marker of emissions from automotive catalytic converters.

Clustering with Mn and Ba has been reported in numerous studies on road dust, being attributed to fuel additives and friction materials (Thorpe & Harrison, 2008; Rauch & Pacyna, 2009). The Fe–Cr–Se cluster reflects the role of Fe–Mn oxides as sorbent phases for toxic metals (Lu et al., 2009). In *urban* aerosols and road sediments, Cr and Se are frequently bound to these phases, and their correlation with Si indicates the mineral support of the particles.

The broad association, including K, Ca, Ti, and REE, is typical of construction dust and resuspended *urban* soils. Vanadium and arsenic, present in the same cluster (pink), are indicators of fossil fuel combustion, especially fuel oil and diesel, a pattern reported in *urban* sediments from port and industrial areas (Pacyna & Pacyna, 2001).

Thus, *urban* marker elements reflect three major sources: road traffic, industrial emissions, and construction dust/atmospheric resuspension (Charlesworth et al., 2011).

Our study highlights *Phragmites australis*'s ability to integrate distinct geochemical features across ecosystem types (*deltaic*, *saline*, *urban*), confirming its role as both a bioindicator and a potential natural filter for lithogenic and anthropogenic elements.

The differences identified between habitats (assessed by ANOSIM, R = 0.0786, p = 0.0179) indicate a distinct elemental structure, mainly driven by the contrast between deltaic and urban ecosystems (p = 0.0015), reflecting the influence of anthropogenic pressure on the chemical composition of plant biomass.

Thus, in *deltaic* ecosystems, a lithogenic contribution was observed, evidenced by the dominance of geogenic elements (Fe > Ba > Mn > Ti; Table 1), resulting from detrital inputs and sediments rich in mineral fractions. The Fe–Ba–Mn–Ti association and the distribution of rare earth elements (REE) (Table 2) reflect the control of the geological substrate and fluvial transport, consistent with the geochemical model of continental sediments described by Taylor & McLennan (1995) and Cullers (2002). The differential fractionation of REE between habitats (Table 2, Figure 7) suggests variations in sedimentary sources and redox conditions (Piper & Bau, 2013).

The association of As–Fe elements in AHC in the *deltaic* environment is due to the role of iron oxides in fixing metalloids in sediments rich in organic matter, a mechanism described by Belzile & Tessier (1990). Therefore, in *deltaic* ecosystems, elemental accumulation in *Phragmites australis* predominantly reflects the natural geochemical background, with a

secondary anthropogenic influence. In contrast, under *saline* conditions, geochemical processes exhibited a distinct element profile absorbed by the reed. The elevated concentrations of Hg, Ba, Sr, and Mo (Table 1 and Table 3) indicate mobilisation and redistribution under high-salinity conditions and variable redox potential. *Saline* AHC revealed three major processes: contaminated detrital input, metal mobilisation under *saline* conditions and mineralisation induced by high salinity. The Cl–Br–Ca–Ba clustering in the dendrogram suggests intense evaporitic processes, described in other *saline* systems (Warren, 2006), with chloride complexation and mobilisation of As and Tl (O'Day et al., 2004), and metal retention on fine particles (Acosta et al., 2023).

The clear separation of the *saline* ecosystem in the PCA for natural elements (Figure 6) and for REE/trace (Figure 7) confirms that salinity constitutes a major geochemical control factor, influencing bioavailability and accumulation mechanisms in reeds.

In *urban* environments, anthropogenic influences were evidenced by obvious enrichments in As, Pb, Mn and Tl (Table 3), as well as in Br (Table 1), suggesting the influence of traffic, fossil fuel combustion and industrial activities, elements also mentioned in other studies (Wei & Yang, 2010). The dominance of Ba > Mn > Ti > Fe (Tables 1-3) indicates a modification of natural ratios by external input. PCA for anthropogenic elements (Figure 2) by the association Sb–Cu–Ni–Mo–Tl–Te reflects sources related to traffic and industry (Thorpe and Harrison, 2008; Rauch & Pacyna, 2009). Also, the presence of Pt in the *urban* cluster supports the presence of a road-pollution marker. The elemental grouping Fe, Cr, Se indicates the involvement of Fe and Mn oxides in the retention and immobilisation of potentially toxic metals in sediment (Lu et al., 2009). The association of V and As suggests external inputs specific to the *urban* environment, including contributions from fossil fuel combustion, which modify the geochemical background and increase metal pressure in the ecosystem (Pacyna & Pacyna, 2001). Thus, the elemental composition of *urban* reeds reflects a mixture of multiple sources: road traffic, industrial emissions and construction dust (Charlesworth et al., 2011).

The ability of *Phragmites australis* to accumulate both lithogenic elements and potentially toxic metals demonstrates its dual role as both a bioindicator of local geochemical conditions, highlighted by the integration of sedimentary and hydrogeochemical signatures and as a biological filter of contaminants, especially in *urban* environments, where it retains heavy metals from the water column and from atmospheric deposits (Alghanem et al., 2024). However, the accumulation of Hg, Pb, As, or Tl in aerial biomass may pose a secondary risk through trophic transfer or biomass decomposition. Therefore, the use of reeds in phytoremediation systems requires biomass management strategies to prevent the reintroduction of contaminants into the biogeochemical cycle. Moderate but statistically significant differences between ecosystems indicate that *Phragmites australis* responds sensitively to variations in anthropogenic pressure and natural geochemical control, confirming its usefulness as a sentinel species in ecological risk assessment.

CONCLUSIONS

Salinity as a major geochemical control factor. In saline ecosystems, the association of Hg, Ba, Sr, and Mo, together with the structure of the agglomerative hierarchical clustering (AHC), highlights the role of salinity-driven geochemical processes. These include element mobilisation, complexation, and evaporite-related precipitation, demonstrating the strong influence of mineralised waters on elemental distribution and bioavailability.

High capacity for bioaccumulation and integration of geochemical signatures. *Phragmites australis* effectively records habitat-specific geochemical characteristics, reflecting both natural variations in substrate composition and the impacts of anthropogenic activities. Its elemental composition provides an integrated signal of environmental conditions across contrasting ecosystems.

Dual role as a bioindicator and natural filter. The species serves not only as a reliable bioindicator of geochemical and environmental conditions but also as a natural biological filter, contributing to the retention and sequestration

of heavy metals, particularly in ecosystems exposed to urban pressures.

Implications for ecological risk. The accumulation of potentially toxic elements such as Hg, Pb, As, and Tl may pose ecological risks through trophic transfer and the subsequent re-release of contaminants into the biogeochemical cycle during biomass decomposition. These findings underscore the need for appropriate management and monitoring strategies in affected ecosystems.

Environmental management applications. The elemental patterns identified in this study provide valuable information for environmental assessment and wetland management, especially in areas influenced by urbanisation or salinisation. Monitoring *Phragmites australis* can serve as an effective early-warning tool for detecting metal contamination, alterations in sediment provenance, and changes in hydrogeochemical conditions, thereby supporting informed conservation and remediation efforts.

ACKNOWLEDGEMENTS

This research was funded by the Institute of Biology Bucharest of Romanian Academy, grant numbers RO1567-IBB02/2026 and RO1567-IBB06/2026.

REFERENCES

Acosta, R., Carol, E., Borzi, G., Cellone, F., & Alvarez, M. D. P. (2023). Factors and processes controlling hydrochemistry and evaporitic deposits in hypersaline wetland–shallow lake systems. *Hydrological Processes, 37*(11), e15031.

Addinsoft. (2014). *XLSTAT Pro: Data analysis and statistical solutions for Microsoft Excel*. Paris, France: Addinsoft.

Alghanem, S. M. S., Alsudays, I. M., Farid, M., Sarfraz, W., Ishaq, H. K., & Farid, S. (2024). Evaluation of heavy metal accumulation and tolerance in oxalic acid-treated Phragmites australis wetlands for textile effluent remediation. *International Journal of Phytoremediation, 26*(13), 2048-2063.

Belzile, N., & Tessier, A. (1990). Interactions between arsenic and iron oxides in lacustrine sediments. *Geochimica et Cosmochimica Acta, 54*(1), 103–109.

Chapligin, V., Dudnikova, T., Chernikova, N., & Fedorenko, A. (2022). Phragmites australis Cav. as a bioindicator of hydromorphic soils pollution with heavy metals and polyaromatic hydrocarbons. *Chemosphere, 307*, 136021

Charlesworth, S., De Miguel, E., & Ordóñez, A. (2011). A review of the distribution of particulate trace elements in urban terrestrial environments and their application to considerations of risk. *Environmental Geochemistry and Health, 33*(2), 103–123.

Chitimus, D., Nedeff, V., Mosnegutu, E., Barsan, N., Irimia, O., & Nedeff, F. (2023). Studies on the accumulation, translocation, and enrichment capacity of soils and the plant species Phragmites australis (common reed) with heavy metals. *Sustainability, 15*(11), 8729.

Clarke, K. R. (1993). Non-parametric multivariate analyses of changes in community structure. *Australian Journal of Ecology, 18*, 117–143.

Cullers, R. L. (2002). Implications of elemental concentrations for provenance, redox conditions, and metamorphic studies of shales and limestones near Pueblo, CO, USA. *Chemical Geology, 191*(4), 305–327.

Förstner, U., & Wittmann, G. T. W. (2012). *Metal pollution in the aquatic environment*. Berlin, Germany: Springer.

Hammer, Ø., Harper, D. A. T., & Ryan, P. D. (2001). PAST: Paleontological statistics software package for education and data analysis. *Palaeontologia Electronica, 4*(1), 1–9.

Hatje, V., Schijf, J., Johannesson, K. H., Andrade, R. C., Caetano, M., Brito, P., Haley, B. A., Lagarde, M., & Jeandel, C. (2024). The global biogeochemical cycle of the rare earth elements. *Global Biogeochemical Cycles, 38*(6).

Holland, H. D., Lazar, B., & McCaffrey, M. A. (1987). The evaporation path of seawater and the coprecipitation of Br^- and K^+ with halite. *Journal of Sedimentary Petrology, 57*(5), 928–937.

Jenkins, R. (1999). *X-ray fluorescence spectrometry*. New York, NY: Wiley.

Jones, B. F., Deocampo, D. M., & Drever, J. I. (2005). Geochemistry of *saline* lakes. In H. D. Holland & K. K. Turekian (Eds.), *Treatise on geochemistry* (Vol. 5, pp. 393–424). Oxford, UK: Elsevier.

Kassambara, A. (2017). *Practical guide to cluster analysis in R: Unsupervised machine learning* (Vol. 1). Paris, France: STHDA.

Legendre, P., & Legendre, L. (2012). *Numerical ecology* (3rd English ed.). Amsterdam, Netherlands: Elsevier.

Lu, X., Wang, L., Li, L. Y., Lei, K., Huang, L., & Kang, D. (2009). Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China. *Journal of Hazardous Materials, 173*(1–3), 744–749.

Mondal, M. N., Horikawa, K., Seki, O., Nejigaki, K., Minami, H., Murayama, M., & Okazaki, Y. (2021). Investigation of adequate calibration methods for X-ray fluorescence core scanning element count data: A case study of a marine sediment piston core from the Gulf of Alaska. *Journal of Marine Science and Engineering, 9*(5), 540.

O'Day, P. A., Vlassopoulos, D., Root, R., & Rivera, N. (2004). The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proceedings of the National Academy of Sciences, 101*(38), 13703–13708.

Pacyna, J. M., & Pacyna, E. G. (2001). An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources. *Environmental Reviews, 9*(4), 269–298.

Piper, D. & Bau, M. (2013) Normalized Rare Earth Elements in Water, Sediments, and Wine: Identifying Sources and Environmental Redox Conditions. *American Journal of Analytical Chemistry, 4*, 69-83. http://dx.doi.org/10.4236/ajac.2013.410A1009

Rauch, S., & Pacyna, J. M. (2009). Earth's global Ag, Al, Cr, Cu, Fe, Ni, Pb, and Zn cycles. *Global Biogeochemical Cycles, 23*(2), GB2007.

Samadi, M. T., Leili, M., Asgari, G., & Chavoshi, S. (2024). The potential of Phragmites australis to bioaccumulation and translocate heavy metals from landfill leachate. *Journal of Water Process Engineering, 64*, 105657.

Song, J., Zhuang, W., & Queiroz, H. M. (2023). Editorial: Biogeochemical processes of micro/trace elements and their impacts on marine ecosystems. *Frontiers in Marine Science, 10*.

Taylor, S. R., & McLennan, S. M. (1995). The geochemical evolution of the continental crust. *Reviews of Geophysics, 33*(2), 241–265.

Thorpe, A., & Harrison, R. M. (2008). Sources and properties of non-exhaust particulate matter from road traffic. *Science of the Total Environment, 400*(1–3), 270–282.

Warren, J. K. (2006). *Evaporites: Sediments, resources and hydrocarbons*. Berlin, Germany: Springer.

Wei, B., & Yang, L. (2010). A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchemical Journal, 94*(2), 99–107.

Weis, J. S., & Weis, P. (2004). Metal uptake, transport and release by wetland plants: Implications for phytoremediation and restoration. *Environment International, 30*(5), 685–700. https://doi.org/10.1016/j.envint.2003.11.002