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Research

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Spatial Distribution of multielements including technology critical elements in sediments of the Danube River

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Abstract

Background: The pollution of the second-longest European river (the river Danube) has been under monitoring and focused on various contaminants including metals/metalloids (Hg, As, Ni, Zn, Cu, Cr, Pb, and Cd), personal care products, technical additives, pesticides, pharmaceuticals, etc. Recent studies show that technology critical elements (TCE) – elements with a high supply risk and economic importance – are becoming emerging pollutants due to their wide application in new technologies. According to the European Union Water Framework Directive, sediments are one of the three major sources of river pollution. This study aims to determine major and trace elements including some TCEs in the Danube River sediment. The concentrations of the targeted elements in the surface sediments were discussed in the sense of the effect of building hydropower dam Iron Gate I and increasing the quantity of sediments in the Iron Gate gorge.

Results: The surface sediments were collected on the Danube River-km 1141 to 864 and three tributaries along this waterway. Two samples of deep sediments were used for comparison. Instrumental Neutron Activation Analysis was applied for quantification of 36 elements, with special attention to selected TCE belonging to lanthanides (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, and Yb). Spatial distribution is discussed (i) in the total pool of all analyzed elements and (ii) only lanthanides. For better understanding and to highlight a hidden relationship between targeted elements, multivariate statistical techniques (cluster analysis and principal component analysis) were applied to analyze the analytical data and to identify possible pollution sources. The obtained results of the targeted elements in the surface sediments were discussed in relation to the influence of hydropower dam Iron Gates I and the increasing quantity of sediments.

Conclusion: Overall results show increasing concentration of almost all investigated elements in the surface sediments from the Danube River-km 1112 to the dam. Sediment od

the River Pek was separated as a location with extreme anthropogenic influence due to close vicinity of the copper mining site.

Keywords: Instrumental Neutron Activation Analysis (INAA); Iron Gate, Lanthanides; Multivariate Analysis; River Danube; Sediments; Technology critical elements (TCE).

Background

Lanthanides (Ln) belong to the group of emerging contaminants with certain aspect of their potential negative effect on environment [1]. Also, Ln are a part of technology critical elements (TCE) e.g. elements with a high supply risk and economic importance, rapidly increased in the last three decades [2]. TCE have been applied in high-technology such as production of electronic devices (e.g. cell phones); in the energy production (hybrid vehicles, wind turbines); in the energy reduction (UV filters in glass, catalyst in chemical processes and catalytic converter); in the energy efficiency (rechargeable batteries, energy-efficient lighting); as a contrast agent in medical imaging (magnetic resonance imaging, radiopharmaceuticals); in the development of advanced weapon systems, etc. [3, 4]. Also, TCE have been used in traditional industries such as petroleum refining, agriculture, metallurgy, and nuclear processing. According to UN Environment Programme [5], future economic development will be oriented toward renewable energy technologies, low carbon public transportation, clean energy vehicles, etc.; so it is directly dependent on various metals including TCEs. It should be stressed, that the permitted concentration of TCEs in the environment are not regulated and monitored, they are trace elements which are detectable with analytical equipment with very low detection limits, and their possible human and environmental toxicity are not clear.

Like many heavy metals, Ln are normal constituents of minerals, and their concentration in the river sediments is related to surrounding geological source. Under natural conditions, Ln may only become available in small amounts via the groundwater and the atmosphere. Recently, Ln, as well as other TCEs, have detected in various environmental compartments and influenced on environmental pollution and human health as a consequence of their increased industrial applications [1]. The sources of increasing concentration of Ln in the environment are domestic, industrial and mine wastewater, e-waste, recycling emissions,

surface run off, and atmospheric deposition [6]. In 1996, Bau and Dulski [7] reported for the first time anthropogenic originated gadolinium in river water from contrast agents for magnetic resonance imaging. Increasing concentrations of Sm and La were detected in the Rhine River derived from the industrial effluent from a facility producing a catalyst for petroleum refining [8]. Increasing concentrations of Ln were found in agricultural soils and human samples in the area of Ln mining and smelting [9], as well as in sediments [10]. Because of the appearance of Ln and the platinum group of elements in higher concentration in the environment compared with their background, these elements were grouped into the fourth group of trace elements that are potentially toxic even at very low concentration and about which not much information is available [11,12]. Although, technological application and research interest for Ln has enhanced, environmental transport and fate, and possible accumulation of these elements and their impact on nature and human health are still limited [1, 13]. Regardless that quantification of TCEs is not covered by the EU monitoring programs, the huge industrial applications of TCEs today and their appearance in different environmental compartments can lead that TCEs could be future candidates for monitoring.

According to the European Union Water Framework Directive, sediments are one of the three major sources of river pollution [14, 15]. Concentrations of the organic and inorganic pollutants adsorbed on sediments of aquatic ecosystems are at higher-level compared with their concentration in corresponding water samples [16]. The adsorption of pollutants on the sediments depends on both the particle size and composition of sediments especially the content of organic carbon [17]. The background level of Ln in river sediments varies significantly and depends mostly on the local geology. The source of metals in aqueous sediments could be both natural and anthropogenic, and it's important to distinguish the geochemical content of sediments from anthropogenic impact in order to further prevent

environmental pollution. Sediments are regarded as a major sink of contaminants, but they can be also a source of contamination in desorption process [18].

The pollution of the second-longest European river (the river Danube) has been under monitoring and focused on emerging contaminants including metals/metalloids (Hg, As, Ni, Zn, Cu, Cr, Pb, and Cd), personal care products, technical additives, pesticides, pharmaceuticals, steroids, perfluorinated compounds [17, 19-24], etc. The biggest hydropower dam and reservoir system along the Danube River is Iron Gate I on Đerdap Gorge, 117 km long. The environmental impact of the dam includes alteration of the hydrological regime on the surface and ground waters and change of the sediment regime. The most important consequence of constructing Iron Gate I is a constant increase of the amount of sediments [25]. The sedimentation rate within the Iron Gate I reservoir is very fast (about 23.3 cm y^{-1}) which implies a high potential of accumulation and as a consequence possibly preservation of pollutants [26]. Because of the above facts, the Iron Gate I has been continuously in research focus due to the significant impact of the hydroelectric power station [24, 26-28]. There are several indications that the largest impoundments of the River Danube (Iron Gates) represent a kind of sink for pollutants [23].

Although the occurrence, distribution, and fate of emerging contaminants including heavy metals in the Danube River have been well examined and monitored, attention should be focused for those elements and compounds which are not monitored but start to appear in the environment and could be considered as future candidates for monitoring. Because of that, this study aims to determine major and trace elements including some TCEs in the Danube River sediment by Instrumental Neutron Activation Analysis (INAA). It should be emphasized that INAA allows simultaneously determining more than 40 elements with high sensitivity due to specific nuclear reaction for each element and low detection limit. INAA has following advantages: a nondestructive method, the sample stays intact and no chemical

separation treatment is involved, simple sample preparation step for solid samples, a small quantity of sample ($\approx 100 \mu\text{g}$), determination of the total element concentration independent of chemical species, real total analysis since the test portion does not have to be dissolved [29]. The concentrations of the targeted elements in the surface sediments were discussed in the sense of the effect of building hydropower dam Iron Gate I and increasing the quantity of sediments in the Iron Gate gorge. Multivariate analysis was applied to explore relationship between variables (concentrations and sample locations).

Materials and methods

Description of the study area

The Danube River (2850 km long with the river basin of 801463 km²) flows through 9 countries and geologically different areas. The Danube River in Serbia is 588 km long, from 1433 km (Hungarian border) to 845 km (border with Bulgaria), and flows through the three geomorphological areas according to Vogel and Pall [30, 31]: Reach 5 (from 1433 to 1202 km, the Pannonian part), Reach 6 (from 1202 to 943 km, Iron Gate gorge) and Reach 7 (from 943 to 845 km, Lowland river). The sample places are located in the Reach 6 and 7. Reach 6 is characterized by the anthropogenic impact of the Iron Gates hydroelectric power plant and the significant inflow of untreated urban (especially from the city of Belgrade) and industrial wastewater, as well as agriculture effluents along upstream of the dam [32]. Reach 7 is characterized as the Lowland river (Aeolian sediments and loess). In the Serbian part, the River Danube receives two large tributaries (Rivers Sava and the Tisza) and several smaller ones (e.g. Velika Morava and Pek). Velika Morava is the last significant right bank tributary before the Iron Gates. River Pek is important because it passing close to the large dumpsites of a copper mine Majdanpek.

The riverbed of the Iron Gate section dominantly consists of coarse sediments and rocks. The river sediment transport depends on the dimension of particles: larger particles (coarse and medium sand) move along the river bed (bed-load), smaller particles (fine sand, silt and clay), which are suspended in water, move with water (as suspended load). The construction of the hydropower dam Iron Gates I and reservoir system along the Danube River (135 km long, upstream of the dam) has been influenced on both the hydrological regime of the surface and ground waters, and amount of sediments [25]. The main effect of hydroelectric plant construction is the increase of sediment accumulation, more than 75% of the incoming sediment remain inside the reservoir [28]. Although, the concentration of the suspended sediment is low ($1 - 100 \text{ g m}^{-3}$), as a consequence of big annual water flow ($110 - 220 \times 10^9 \text{ m}^3$), the quantity of sediments reaches $7 - 10 \times 10^6$ tons [25]. The largest quantity of sediments (up to 10 m high) was accumulated three years after the construction of the dam (1972-1974) and located between 970 and 1003 km of the River Danube. After that time, the sedimentation zone moved towards the dam [25]. These sediments are built from suspended sediments of the Danube (39%), the Tisza (26%), the Sava (21%) and the Velika Morava (14%).

Sampling and sampling locations

The samples were taken at 8 sites along the Danube River from 1141 to 864 km and in 3 main tributaries belonging to the middle Danube basin (Fig.1 and Table 1). Six samples belong to Reach 6 and two samples to Reach 7. Additionally, we subdivided Reach 6 in the Upper stream from Iron Gate I and Iron Gate I according to a different rate of sediment accumulation. Since there is no significant accumulation of sediments in the Upper stream from Iron Gate I. Surface sediments were collected from the surface of the river bottom at the central and the deepest part using an Ekman grab sampler in April 2016. The sediment samples are very fine with a strong muddy smell. Deep river sediment (1.5 -2 m deep) and

river bed (7.2 -7.3 m deep) were collected at 1112 km of the River Danube. The samples (about 1 kg each) were transferred into the plastic containers and placed in a cooler for transport to the laboratory. The samples were mixed and air-dried in a thin layer in the dark at room temperature (23 ± 1 °C). After drying, the samples were homogenized using a pestle and mortar and sieved through a 1-mm sieve to ensure sample homogeneity.

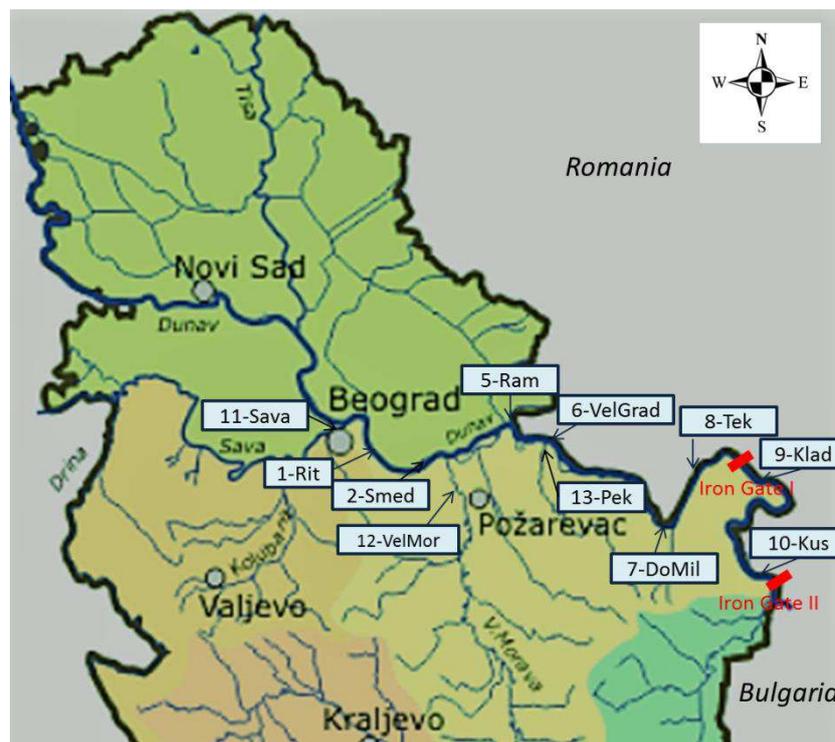


Figure 1. Map of the Danube River and its tributaries in the Republic of Serbia (sample locations are given in squares).

Table 1. Properties of the sample locations.

Sample code	River	River, km	Place	Features (Reach*)
1-Rit	Danube	1141	Ritopek	Upper stream from
2-SmedDS	1.5 - 2.0 m deep	1112	Smederevo	Iron Gate I
3-SmedRB	7.2 - 7.3 m deep	1112	Smederevo	(Reach 6)
4-Smed	Danube	1112	Smederevo	
5-Ram	Danube	1072	Ram	
6-VelGrad	Danube	1059	V. Gradiste	Iron Gate I
7-DoMil	Danube	991	D. Milanovac	(Reach 6)
8-Tek	Danube	956	Tekija	
9-Klad	Danube	934	Kladovo	Iron Gate II
10-Kus	Danube	864	Kusjak	(Reach 7)
11-Sava	Sava	5	Belgrade	
12-VelMor	V. Morava	2	-	Tributaries
13-Pek	Pek	0	-	

*Geo-morphological reaches of the river Danube according to Vogel and Pall [30]

Quantification of the selected elements in the sediments

All samples are analyzed applying INAA. The major elements (Al, Ca, Fe, K, Na, Ti, Mg, and Mn); trace elements (Ba, Zn, Cr, Sr, V, Rb, Ni, Cu, Co, As, Sc, Th, Cs, Hf, Sb, U, W, Ta); and lanthanides (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb) were quantified. The analytical procedure based on INAA were been described in detail elsewhere [33, 34]. Irradiations of the samples were performed at the pulsed reactor IBR 2 (Frank Laboratory of Neutron Physics - FLNP, Joint Institute of Nuclear research - JINR, Dubna, Russian Federation) using thermal or epithermal neutrons [33].

Samples of sediments (≈ 100 mg each) were dried to constant mass at 100 °C and wrapped in polyetheneoraluminium foils for short and long-term irradiations, respectively. For the determination of short-lived isotopes, samples were irradiated for 60 s and measured for 15 min. For quantification of long-lived isotopes, samples were irradiated for 4 days,

repacked and measured twice, after 4–5 days and after 20–23 days, with acquisition lasting for 30 min and 1.5 h, respectively. The nuclides of interest were determined by gamma rays spectroscopy using a high-resolution germanium detector (Canberra GC5519/7500SL). Data processing and determination of concentrations of the studied elements were performed using software developed in FLNP JINR [35]. The accuracy of the applied method was checked and confirmed by the analysis of certified reference materials (CRM): IRMM BCR 667 (ESTUARINE SEDIMENT), NIST SRMs 2709 (Trace elements in soil) and 1632c (Trace elements in coal (Bituminous)). All measurements were done in triplicate, and the mean concentration was used for further analyses. Relative standard deviations of measurements ranges from 3.8 to 14.7%, except for Gd and Dy (RSD = 25%).

Quality assurance

Neutron activation analysis is based on the determination of the concentration of the analyzed element from the measured induced activity in the characteristic range of energy. It is possible to define the activity based on nuclear constants (absolute INAA). In this study, we used a relative INAA when the same conditions for irradiation of samples and standards of identical weight were applied and the concentration of analyzed element calculated according to the equation [33]:

$$C_{sample} = C_{stand} \frac{A_{sample}}{A_{stand}} \quad (1)$$

where A_{sample} and A_{stand} are activities measured in samples and standards, C_{sample} and C_{stand} are corresponding concentrations.

The reference material for irradiation is prepared using the same procedure as the samples. CRM is used for both quality assurance and as a standard (calibrator) in INAA relative method. The chemical matrix effect is known to be significant sources of error in many instrumental chemical analysis, but it is insignificant in INAA [31].

Determination of total organic carbon (TOC)

TOC was determined by a semi-quantitative method which involves thermal destruction of all organic matter in the samples. Sample of known weights (previously heated at 100°C) was placed in a ceramic vessel and heated at 400 °C until the constant weight (2h). Then, samples were cooled in a desiccator and weighted at analytical balance. TOC is calculated as the difference between the initial and final sample weight [36].

Multivariate analysis

Multivariate analysis and chemometric methods were applied to better understand the spatial distribution of the quantified elements and to highlight hidden relationship between variables, *i.e.* elements and sample locations. A data matrix, with locations presented in rows and elements as descriptors in columns, was built for further multivariate analysis [37]. At the beginning, the Ryan-Joiner test was applied to examine whether or not the experimental data follow a normal distribution. It is important to mention that variables (features) must be standardized (transformed) for further processing because of different units and ranges of measurements. The mean value and standard deviation are frequently used for this purpose and each value (x_i) is replaced by the corresponding z_i value using the expression:

$$z_i = \frac{x_i - \bar{x}}{SD} \quad (2)$$

where z_i is the autoscaled value of x_i and SD is the standard deviation of variable x .

Then, a data matrix, with locations presented in rows and autoscaled values of elements' concentration as descriptors in columns, was built for further multivariate analysis. The obtained data set was subjected to correlation analysis. Exploratory approach of Factor analysis was applied.

Factor analysis

Factor analysis is one of the often-used methods for analyzing multivariate data. It explains observed multivariate data in terms of the linear relationships between a smaller number of unobserved variables, called latent variables or factors. Factor Analysis is based on an assumption that these factors exist and that their number is exactly known, so the method is reliable only if the modeled system is well understood. Contrary to this, principal component analysis does not rely on such assumptions about covariance matrix and uses linear combinations of the observed variables. We employed both methods to cross check the produced results [37].

An initial statistics of the correlation matrix was done using Eigen analysis. Eigen values are calculated according to the expression:

$$R \cdot e_1 = \lambda \cdot e_1 \quad (3)$$

where R is the correlation matrix, e are eigen vectors and λ are eigen values.

The eigen values are measure of the extracted variance from the total feature variance s^2 total. The sum of the eigenvalues is equal to the number of features (variables). The total number of features describes the variance of the full data set (numerical patterns – loadings). We gave an advantage to Kaiser criterion over Catell's and retained only the first components with subsequent eigenvalues less than one since they accounted for a high percentage of the determinable variance.

After extraction of the factors, the obtained matrix will show the significant loadings in each factor and present the combination of variables. That means that principal component analysis (PCA) transformed a set of possibly correlated random variables into a set of uncorrelated variables, called principal components. Using PCA, the reduction of the data set is realized by transforming the data into orthogonal components that are linear combinations of the original variables. This way, by compression, PCA reduces the complexity of high-

dimensional data while retaining its patterns. Furthermore, when the obtained matrix contained too many medium factor loadings it appeared to be difficult to interpret the solution of the factors. That's why we applied a rotation of the coordinate system of factors since it does not affect the position of the objects (locations) relative to each other, but will simplify the structure of the factors. Among several available numeric transformation algorithms we selected varimax because it minimized the number of variables with high absolute values of factor loadings.

Cluster analysis

Another unsupervised learning method that belongs to Factorial methods is cluster analysis (CA) [37]. This method is very powerful in visualizing structural similarities (groups, classes) in the data and can be seen as a pattern cognition method.

For finding structures in a data set, there is a necessity for similarity (or distance). This is derived from geometry. The Euclidean distance of any two objects A and B is calculated according to expression:

$$d(i, k) = \sqrt{\sum_{i=1}^m (x_{ij} - x_{kj})^2} \quad (4)$$

where m is the number of features (variables) and d(i,k) is the Euclidean distance of any two objects A and B. In the obtained distance matrix the correlation coefficients appear as a measure of similarities of each pair of features, instead of distances between objects. In selecting strategy, hierarchical technique was applied because the typical output of a hierarchical clustering method is dendrogram, as very helpful in interpretation of our results. As the mode of the agglomerative hierarchical method the Ward linkage was selected.

Software

Minitab 16.1.0.(2010, Minitab Inc., State College, PA)for Windows software package was used.

Results and discussion

Thirty-six elements were determined in the analyzed sediments of the River Danube and three tributaries applying INAA. All measurement data including the descriptive statistic results (mean concentration and standard deviation) are given in Table S1 in the supplementary material. The concentrations of studied elements in the monitoring sediments are very variable between the sample locations with relative standard deviation from 12.5% to 140%. The highest variability (RSD > 30) was found for Cu, Na, Ca, Zn, Cr, Ni, As, Cs, and Sb.

Major, minor and trace elements composition in the surface and deep sediments

The most abundant metals in the sediments that we found are: Al (4.9 – 9.9%), Ca (2.3– 9.9%), Fe (3.09– 4.8%), K (1.3 – 2.2%), Na (0.6 – 1.8%), Ti (0.33 – 0.59%), Mg (0.24 – 0.53%), and Mn (0.07– 0.36%) (Table S1(a) in the supplementary material). The highest variability in the group of major elements (RSD > 30) was observed for Ca and Na e.g. Ca concentration is significantly higher in the samples 11-Sava and 1-Rit which are close each other and landscape is very similar. The highest concentration of Na and the lowest concentration of Ca were found in two tributaries (12-VelMor and 13-Pek). The highest Al content (higher than 2 standard deviations (SD) comparing to mean concentration) was found in the monitoring places where the sediments deposition is the highest (6-VelGrad and 7-DoMil in Iron Gates I). Also, the concentrations of Ti and Mn are the highest in the samples belonging to the Iron Gate I. Lower concentrations for almost all major elements were found at sample 1-Rit which is far away from Iron Gates I and at the border with Reach 5 which has different geochemical content compare to other investigated Danube sediments. Only, Fe and K are homogeneously distributed in the surface sediments of the Danube, while their concentrations are lower in tributaries and deep sediments. Analysis of the deep sediments (2-SmedDS and 3-SmedRB)

shows lower concentration levels for almost all determined elements. Only Ca and TOC are particularly pronounced in the sample at a depth of 7 m (3-SmedRB) due to long-time precipitation of the residues of plants and animals decay. Also, values of TOC (Table S1(a) in the supplementary material) are higher in the samples belong to Iron Gate I comparing to other surface samples as effect of the sediment retention.

Concentrations of all other measured elements are below 0.1% (minor and trace elements, Table S1(b) in the supplementary material). Spatial distribution of the elements with variability within groups higher than 30% is presented at Fig. 2. The extremely high concentration of copper, higher than remediation value prescribed by national law (Table S2 in the supplementary material) [39], was found in the sediments of river Pek (13-Pek). This river flows near the Majdanpek copper mine and that is the reason for the high concentration of Cu. Also, higher concentration of Cu was found in samples 7-DoMil and 8-Tek which lie behind the mouth of the Pek River into the Danube. Zink concentration in samples 4-Smed and 12-VelMor exceed the maximum allows values, therefore in all other samples are higher than target values but bellow the maximum allows values (Table S2 in the supplementary material) [38]. We can see from Fig. 2, that concentration of Zn, Cr, and As in the sample 4-Smed are 2-9 times higher than in the sample 3-SmedRB which can be assumed as intact. This result indicates an anthropological influence probably derived from a steel processing plant which is located near the town of Smederevo. Arsenic is mainly equally distributed in the surface sediments, but the difference between them and dipper sediment is the highest observed. It should be noted that the concentration of As is bellowed target values in all samples. The concentration of Ni is above maximal recommended values in all samples except 13-Pek, but lower than remediation value [38]. Only the concentrations of Sb in the 3-SmedRB sample are higher compared to the surface sediments. Other trace elements (Sc, V, Rb, Sr, Cs, Ba, Hf, W, and Th) are very uniform in the sediment belonging to Reaches 6 and

7, whereas the concentration is lower in deep sediments and in tributaries. Ta and U represent elements with the lowest variability among all investigated samples.

Comparison the heavy metals concentrations in different time periods from 1985 to 2016 (Table S3 in the supplementary material) shows a trend of increasing concentrations of Fe, Mn, Zn, Cr, Ni and Cu in the investigated surface sediments [17]. The increase in Cr, which is 5 times higher in 2016 than in 2002, is especially pronounced and indicates an anthropological influence.

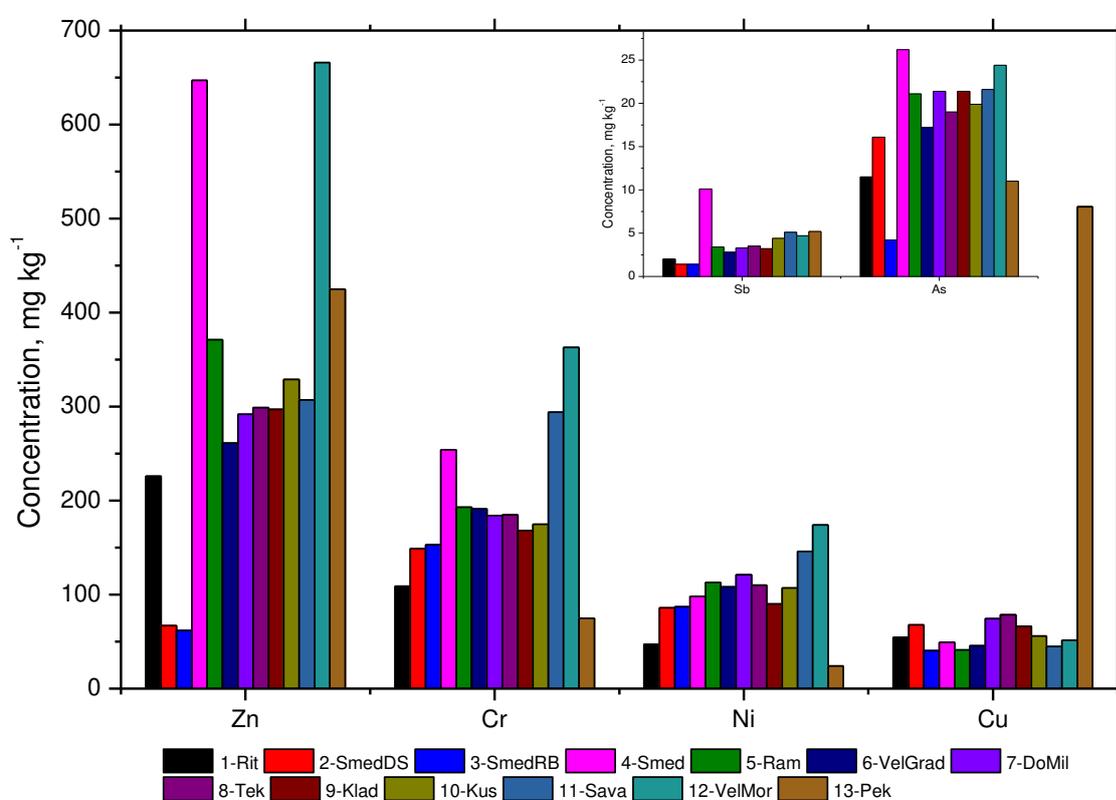


Figure 2. Graphical presentation of spatial distribution of the elements with variability within group of minor and trace elements higher than 30%.

Composition of the studied lanthanides in the surface and deep sediments

Spatial distribution of lanthanides in the investigated sediments is given in Fig. S1 in the the supplementary material. The concentration range of lanthanides is brode and ranges from 0.3 to 71 mg kg⁻¹. Based on the descriptive statistic of the investigated lanthanides (Table S1 (c)

in the supplementary material), estimated RSD range was from 10.5 to 29.6%. Yb and Tb are the most uniformly distributed elements in the studied samples with RSD 10.5% and 12%, respectively. Contrary, Nd, Sm and Dy are the elements with the highest variability in the studied sediments with RSD > 20%.

Given the large difference in Ln concentrations in nature compartment, a pattern of the rare earth elements is usually described by normalizing these elements concentrations in the sample to those of the crustal abundance of the earth. Fig. 3 shows spatial distribution of the studied lanthanides depicted as relative concentration against either Upper crust concentrations taken from Taylor and McLennan [39] or concentration in sample 3-SmedRB. The second approach is based on an assumption that sample 3-SmedRB is unpolluted because was dig on 7.2 – 7.3 m deep, so the ratio of $C_{\text{sediment}}/C_{3\text{-SmedRB}}$ was used to highlight the possibility of anthropological influence.

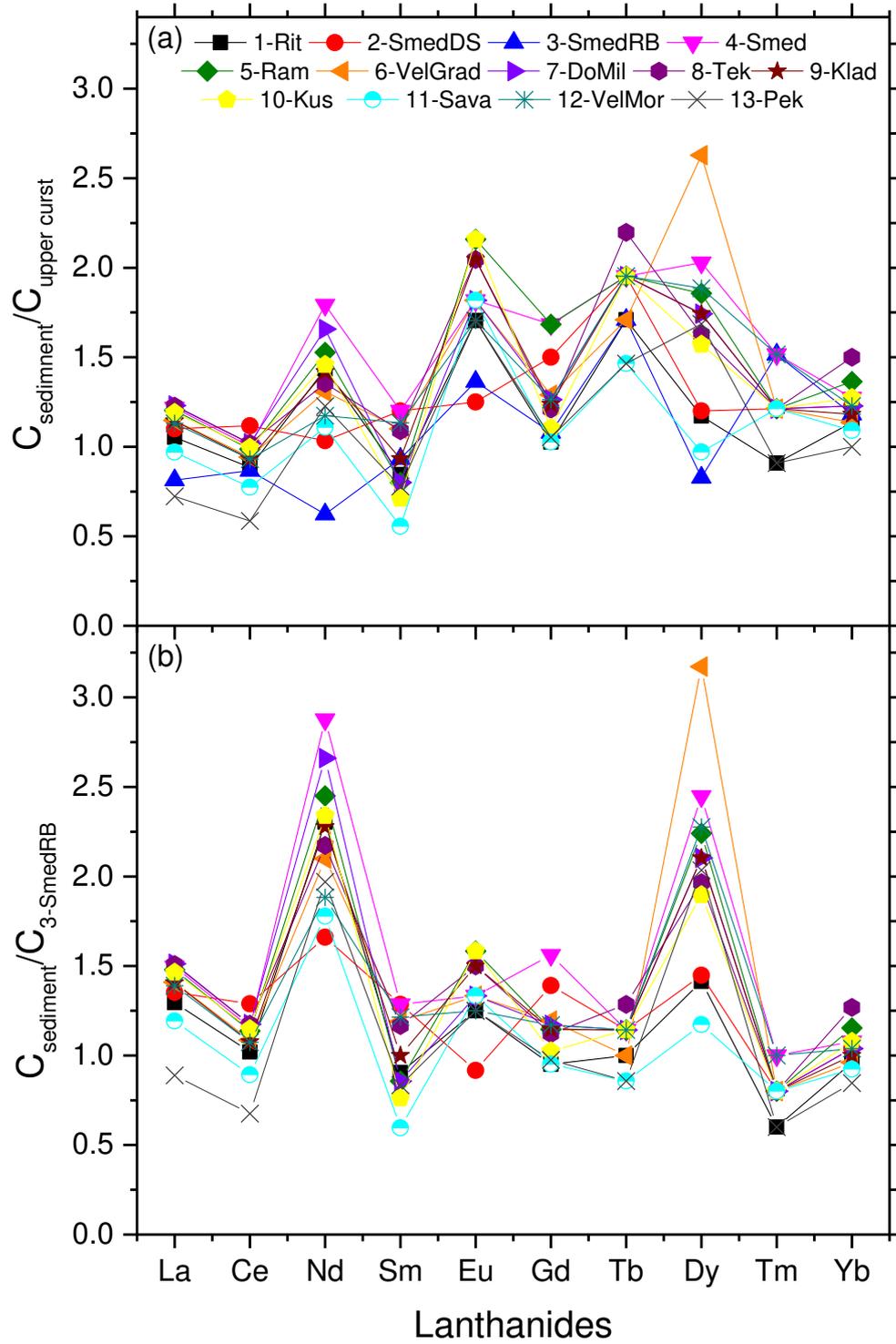


Figure 3. Spatial distribution of lanthanides depicted as a relative concentration in surface sediment sample against (a) Upper crust concentrations [39] or (b) concentration in sample 3-SmedRB.

The spatial distribution of Ln normalized against upper crust concentration ranges from 0.6 to 2.6 (Fig. 3a). Similar distribution was found for almost all Ln in the sediments. The normalized values > 1.5 were found for Nd, Eu, Tb and Dy in surface sediments located in Iron Gate which is an indication of the positive anomaly for these elements. Mean normalized values of sample 3-SmedRB is 1.12 ± 0.35 . Because of that, we choose this sample as pristine and in further work applied for normalization of other samples.

Fig. 3b depicts the spatial distribution of relative concentration of Ln in the surface sediments calculated against their concentration into deep river sediments (3-SmedRB). Comparison of Figs. 3 (a) and (b) it is clear that the spatial distribution of Ln differs in the case of different applied reference values. In the second approach (Fig. 3b), high homogeneity for almost all samples was obtained. The largest differences were observed for Nd and Dy, even 3 times higher for the sample 6-VelGrad (Fig 3b). It is obvious that the second approach, which resulted in much better outcome in terms of uniformity and clarity due to similar matrix composition, confirms that potentially unpolluted sample of river bed (sampled at 7m) is a better choice for matrix match.

Chemometric evaluation of total pool of measurements for all elements

Given that environmental data are strongly characterized by inherent variability. the nature of the study objectives in this work is of multivariate nature, in following part we applied multivariate statistical analysis approach. PCA and CA have been applied to assess the level of heavy metals in sediments [40, 41], soil [42], etc. PCA is used to reduce dataset to a small number of independent components for analyzing relationships among the observed variables. CA has been applied to identify different geochemical groups, clustering the samples on the basis of the similarities of their chemical properties [43].

The data set of concentration measurements was subjected to a PCA in order to decrease the number of descriptors responsible for the highest percentage of the total variance of the

experimental data. The reduction of high dimensional feature space, to one which can be explained with fewer variables, is important to highlight the significant correlations, usually hidden in the original dataset. When PCA was applied to the autoscaled data matrix, with Eigen analysis as an initial (Table S4 and Fig. S2 in the supplementary material), six Principal Components (PCs) were extracted according to the Kaiser criterion which explains upto 93.80% of variance. Thus, the true dimensionality of the descriptorspace is six. As a result, we have got a space that can be described with six factors. Features with high positive or negative loadings essentially determine the factor. Since there were too many medium factor loadings in the first (unrotated) matrix for a solution of the factor, the mathematical rotation appeared as necessary to simplify the structure of the factors for a better interpretation. We applied the Varimax rotation (Table S5 in the supplementary material).

PCA (Fig. 4a) shows two groupings. The first group, to the left, five locations in the direction of Na, Cu and Ca vectors. These are differentiated by higher Cu (13-Pek) and high Ca (1-Rit, 2-SmedDS, and 3-SmedRB). The elevated Cu derives from close vicinity of the copper mine. The second group, to the right, in the direction of increased lanthanides and all other investigated elements lies in the area closer to Iron Gates Dam. The elevated concentrations of these elements can be explained by the increasing deposition of sediments.

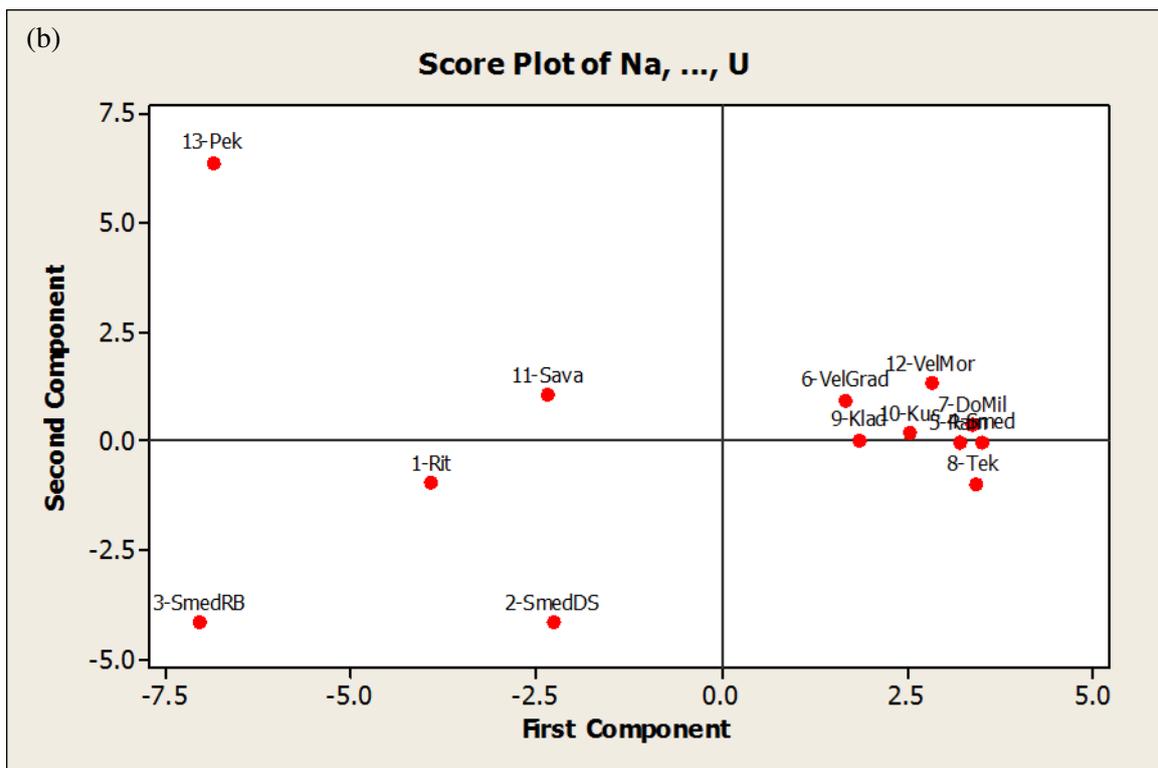
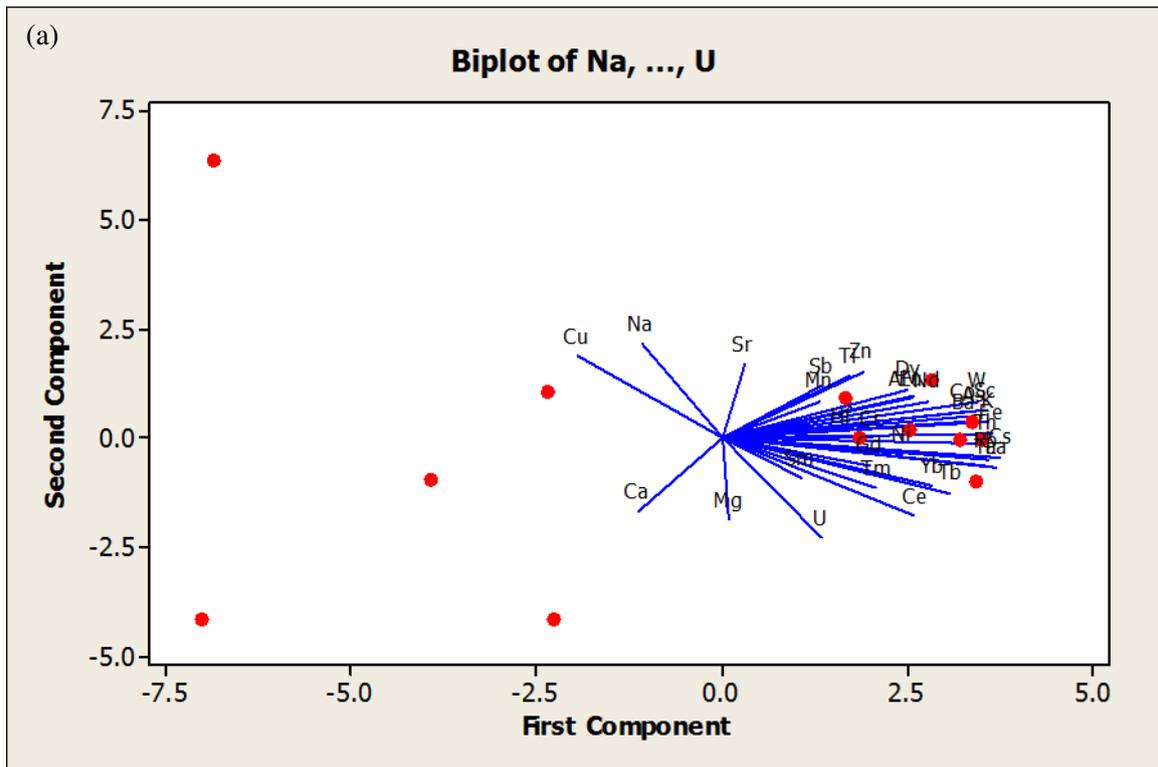


Figure 4. Score plot of PCA in analysis of total pool of results in regard to elements as (a) vectors, and (b) locations.

Going further with chemometric evaluation to identify relatively similar i.e. homogenous groups of objects (locations) in the space of measured features (elements), a hierarchical agglomerative cluster analysis (HCA) was performed. Ward's method, as an amalgamation rule, was applied on standardized concentrations of the elements and the Euclidian distance as a measure of the proximity between samples. Well-differentiated corresponding dendrogram is shown in Fig. 5. The first cluster comprises sub-cluster with samples 1-Rit and 11-Sava, geographically close to each other and sample from location 3-SmedRB, with similar concentrations for majority of elements (Table S1 in the supplementary material). It should be emphasized that 3-SmedRB is distanced from all other samples (Fig 4b) because its only sample which excavated at a depth of 7.2 m. The second cluster comprises the samples belonging to surface sediments of the River Danube from 1112 to 934 km which is characterized with increased accumulation due to the building of the dam. Sample 2-SmedDS is a bit separated (Fig 4b) and also at the edge of the 2nd cluster (Fig. 5) because the sampling was done from a deeper level (2 m). Samples from locations 10-Kus and 12-VelMor belong to the third cluster with an assumption of similar concentrations for Ca, V and Sb (Table S1 in the supplementary material). Location 13-Pek is already discussed concerning the extremely high concentration of Cu due to the vicinity of the copper mining site. In certain cases of chemometric evaluation, such extreme values are being discarded as outliers to enable further modeling, but in this work, we retained it based on knowledge of its source.

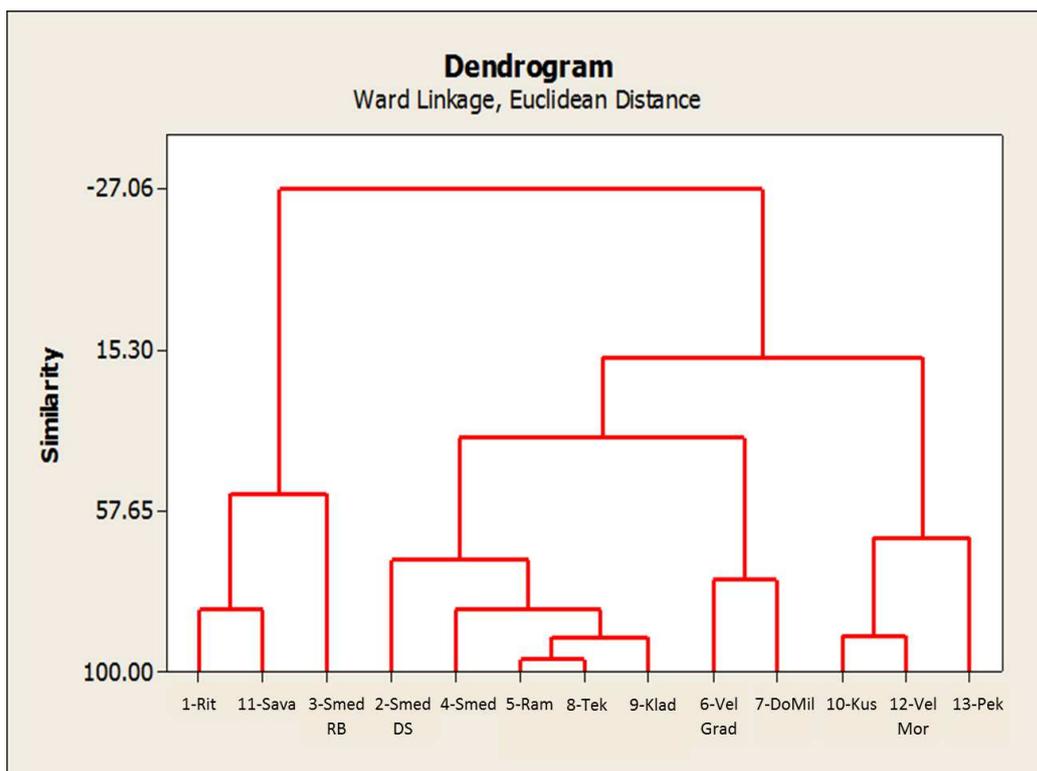


Figure 5.Dendrogram presenting hierarchical clustering of sampling locations. Analysis includes all determined elements.

Chemometric evaluation of the studied lanthanides

In order to get a better insight into the lanthanides profile in analyzed samples, the dataset was subjected to the second round of PCA. Score plot of the studied lanthanides is given in Fig. S3 in the supplementary material. As afore mentioned, the sample 3-SmedRB from a deep river bad (7.2 m deep) is separated from other samples on a score plot of lanthanides and because of that was assumed as intact and unpolluted (without anthropological influence). From that reason, in further study, the relative concentration of lanthanides against the concentrations of lanthanides in the sample 3-SmedRB were used to the third round of PCA (Fig. 6).

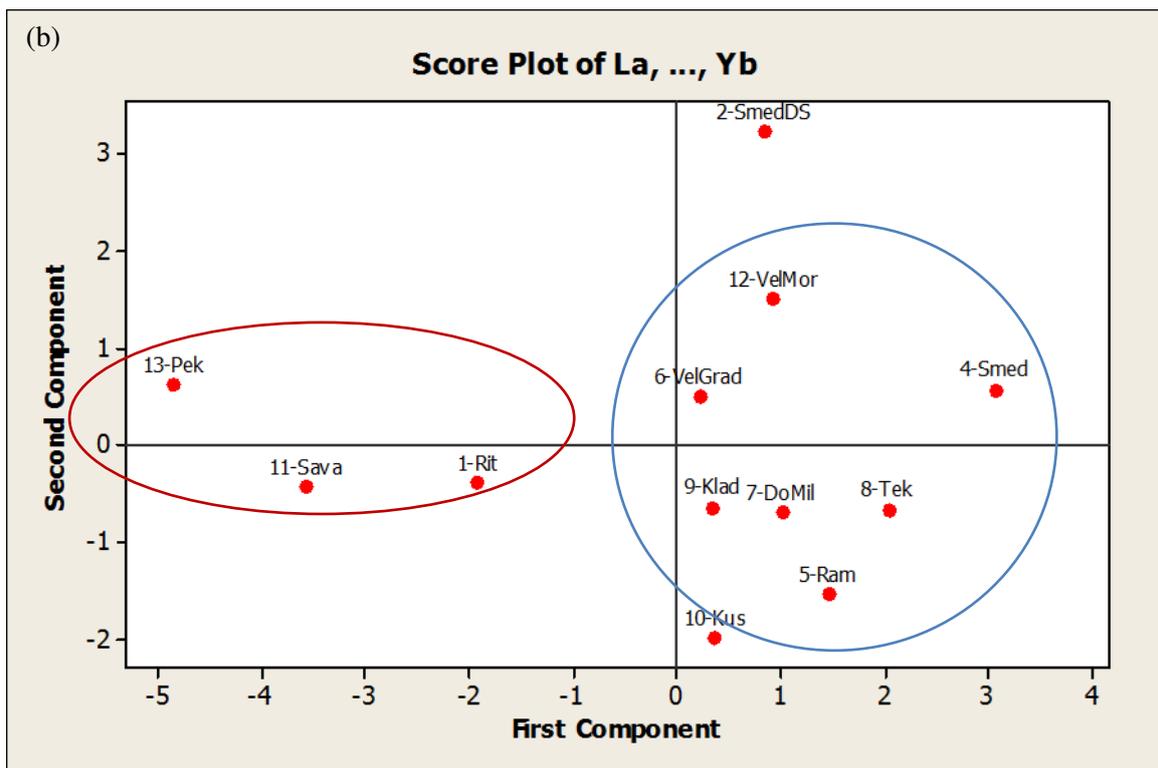
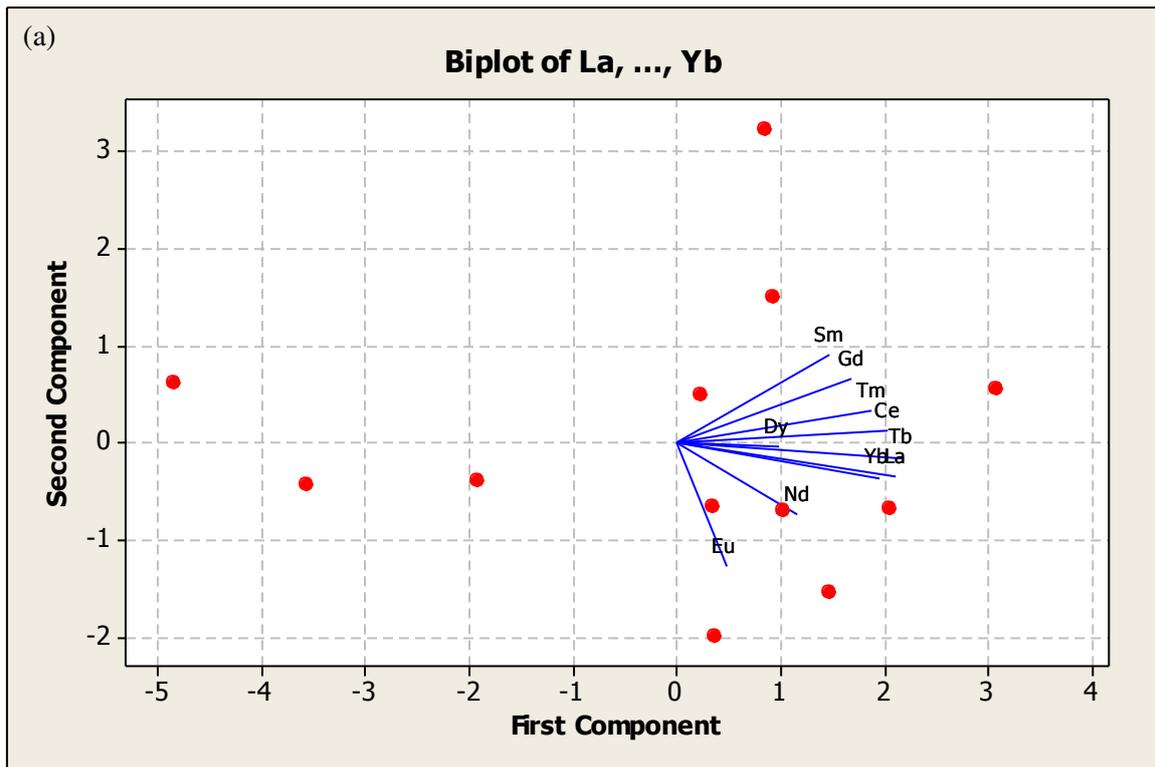


Figure 6. Score plot of PCA of relative concentrations of lanthanides in regard to elements as (a) variables, and (b) locations as objects.

Grouping of samples 1-Rit, 11-Sava and 13-Pek (red circle) is obviously the result of lower total concentration of all lanthanides, presented as ΣLn in Table S1c in the supplementary material. Another group (blue circle) is represented by those samples with increased concentration of lanthanides. The sample 2-SmedDS, which was excavated at a depth of 2 m, exhibits the lowest variability of lanthanides in comparison with other samples (Fig. 3), and from that reason it is bit separated from other locations in Fig. 6.

CONCLUSION

This study provides a detailed analysis of 36 elements in surface sediments of the River Danube collected from 1141 to 864 km and three major tributaries on this stream performed by INAA. Although INAA cannot be considered as routine analysis because of the main disadvantages – need for a nuclear reactor and handling and safe disposal of radioactive materials, but is important comparative analytic method. The studied elements exhibited high spatial variabilities, with the highest concentrations in the samples located in the Iron Gate I region, where the accumulation of sediments is pronounced as a consequence of building the dam. The extremely high concentration of copper, higher than remediation value prescribed by national law, was found in the sediments of river Pek that flows near the Majdanpek copper mine. Also, concentrations of Zn, Cr, and As in the sample 4-Smed are 2-9 times higher than in the sample 3-SmedRB which was assumed as intact. This result indicates an anthropological influence probably derived from a steel processing plant which is located near the town of Smederevo. The concentration of Ni is above maximal recommended values in all samples except 13-Pek, but lower than remediation value. We found that the level of some metals (Fe, Mn, Zn, Cr, Ni and Mn) is significantly higher (up to five times for Cr) comparing to earlier data due to increasing accumulation of sediments as the consequence of building Iron gate I dam.

Bearing in mind high environmental variability due to numerous impacts, multivariate approach was applied. Six PCA components explained 93.80% of variance. Varimax rotation of the obtained matrix simplified additionally the structure of factors by discarding those with medium loadings. The well-differentiated dendrogram was obtained by a hierarchical agglomerative Cluster Analysis. It noticed that variability of sample location resulted in the structure of clusters. For example, the first cluster comprises sub-cluster with samples 1-Rit and 11-Sava, geographically close to each other and sample from location 3-SmedRB, with similar concentrations for the majority of elements. The second cluster comprises the samples belonging to surface sediments of the Iron gate 1 which is characterized by increased accumulation of sediments as the consequence of building the dam. Both PCA and CA separated 13-Pek due to the extremely high concentration of Cu due to the vicinity of the copper mining site with increased accumulation.

The concentrations of the studied lanthanides in the Danube surface and deep sediments were determined for the first time, and the obtained data are important in the creation of a database necessary for tracking anthropogenic intrusion on the content of natural objects. We found variability in the results depending on the approach of calculation of the relative value of lanthanide. The deviation (> 1.5) was found for Eu, Tb and Dy in almost all surface sediments of the River Danube which is an indication of the positive anomaly for these elements. The largest difference was observed for Nd and Dy, even 3 times higher for the sample 6-VelGrad. The following step with lanthanides profile chemometric evaluation resulted in: firstly, in the clear distinction of the sample 3-SmedRB from a deep river bed, assuming it as intact and unpolluted (without anthropological influence) and secondly, grouping of those sites with lower and increased total concentration of all lanthanides.

Considering the wide application of lanthanides as technological critical elements and ecological importance which is still not well estimated, further work should be a focus on

periodic monitoring of these elements in surface sediments as well as corresponding river water to deeper understand their sources and fate in environment. It is necessary to emphasize the importance of a large multi-element approach in the study of lanthanides. Having reliable data on the content of heavy metals that are much better studied, it is possible to more correctly identify the sources of lanthanides.

List of abbreviations

Ln: Lanthanides; TCE: Technology critical elements; INAA: Instrumental Neutron Activation Analysis; FLNP: Frank Laboratory of Neutron Physics; FLNP: Frank Laboratory of Neutron Physics; JINR: Joint Institute of Nuclear research; CRM: Certified reference materials; RSD: Relative standard deviation; TOC: Total organic carbon; SD: Standard deviation; PCA: Principal component analysis; CA: Cluster analysis; PCs: Principal components.

Declarations

The authors declare that this work is original and has not been published elsewhere, nor is it currently under consideration for publication elsewhere.

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

The datasets obtained and analyzed in the current study are available from the corresponding author on reasonable request.

Competing interest

The authors declare that they have no competing interests.

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Authors' contributions

OAC was involved in the experiments and manuscript writing. RB and SR were responsible for the data analysis. AP collected samples. TTP designed the study and corrected of the manuscript.

All authors read and approved the final manuscript.

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Figures

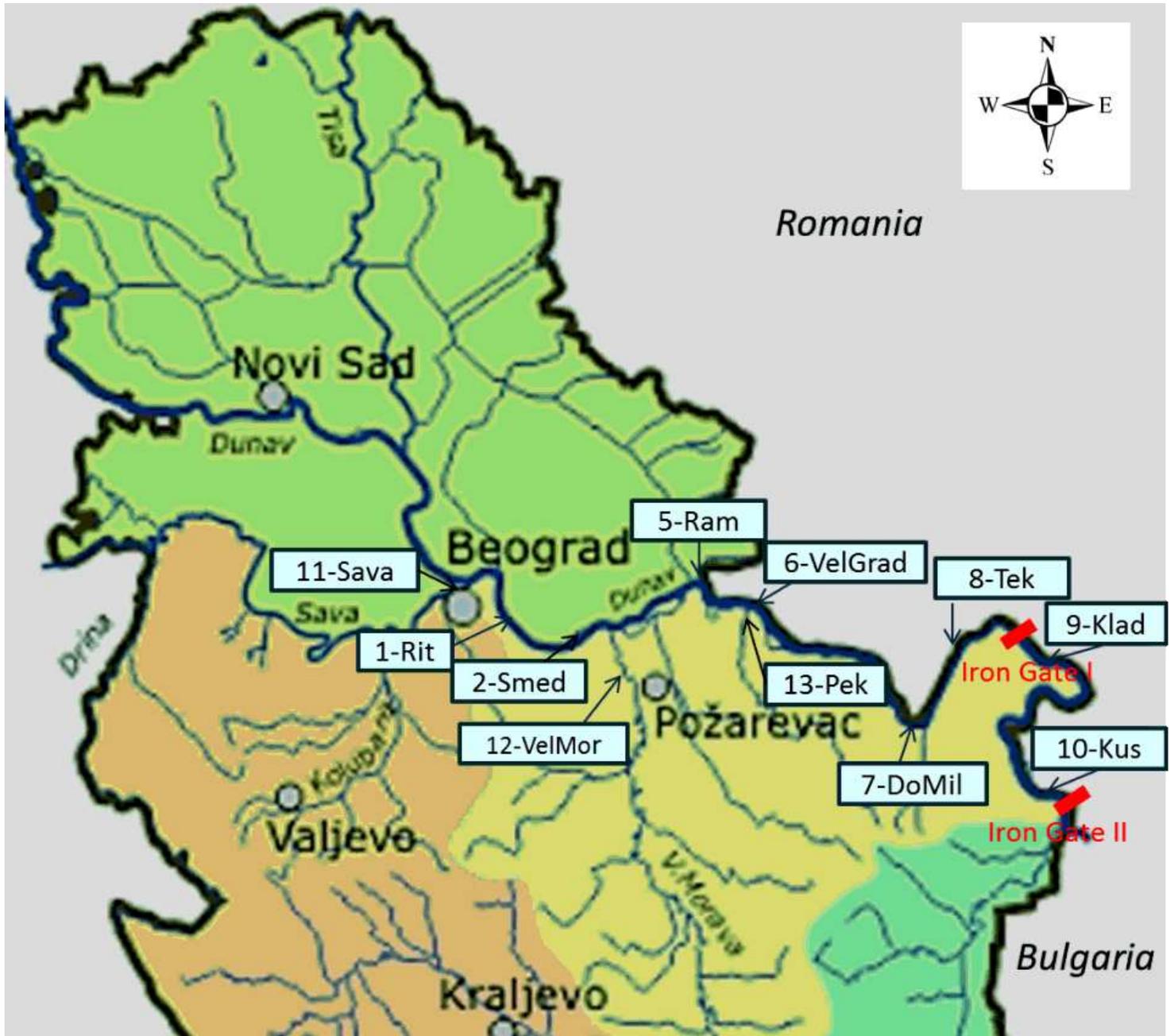


Figure 1

Map of the Danube River and its tributaries in the Republic of Serbia (sample locations are given in squares).

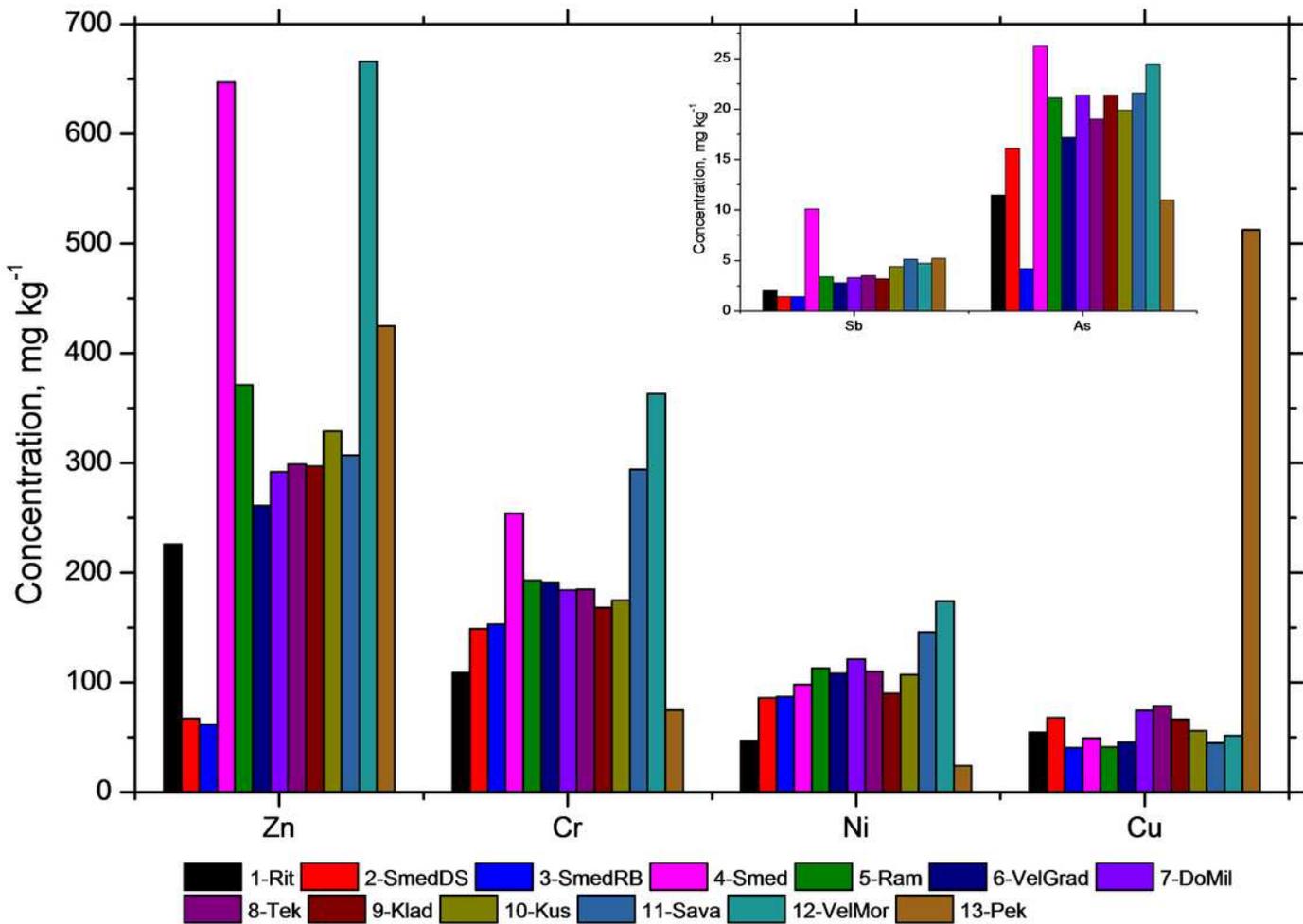


Figure 2

Graphical presentation of spatial distribution of the elements with variability within group of minor and trace elements higher than 30%.

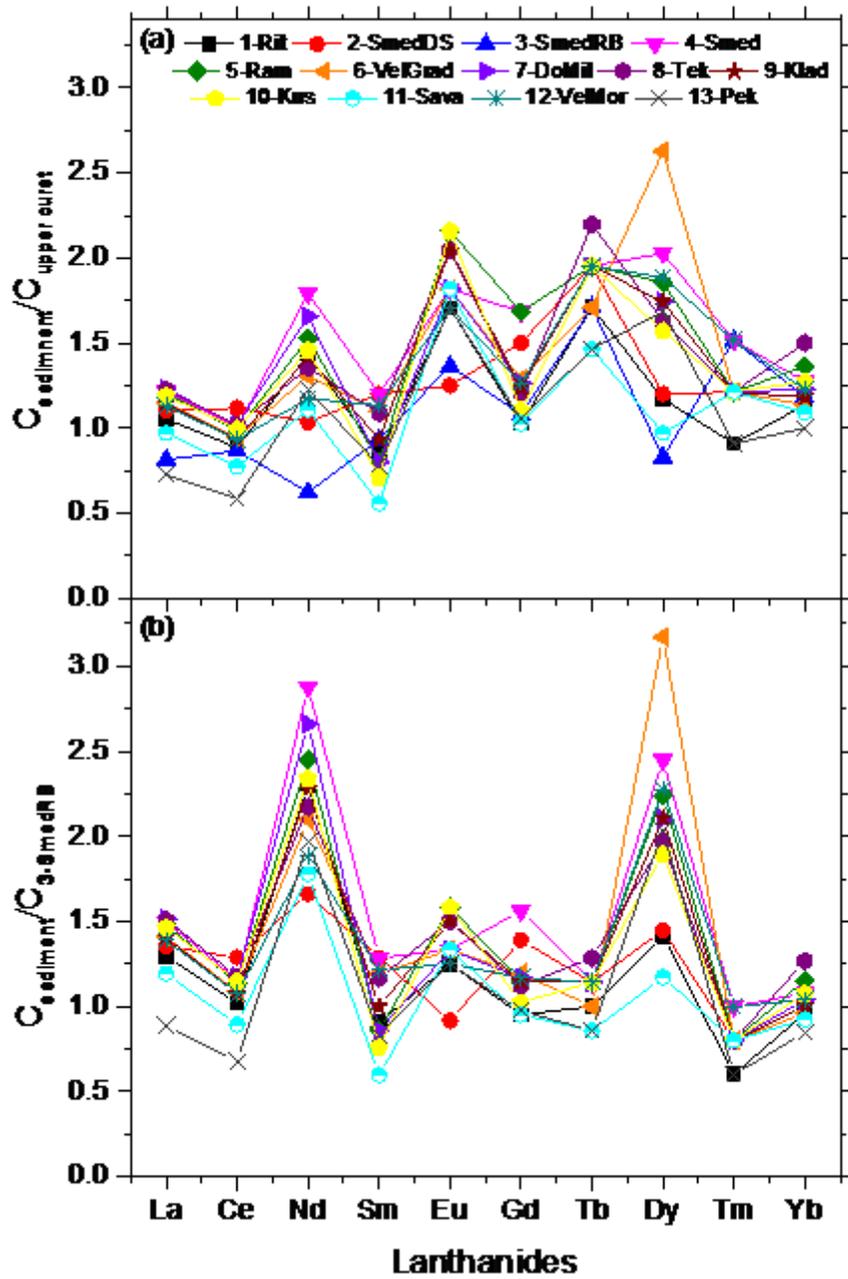


Figure 3

Spatial distribution of lanthanides depicted as a relative concentration in surface sediment sample against (a) Upper crust concentrations [39] or (b) concentration in sample 3-SmedRB.

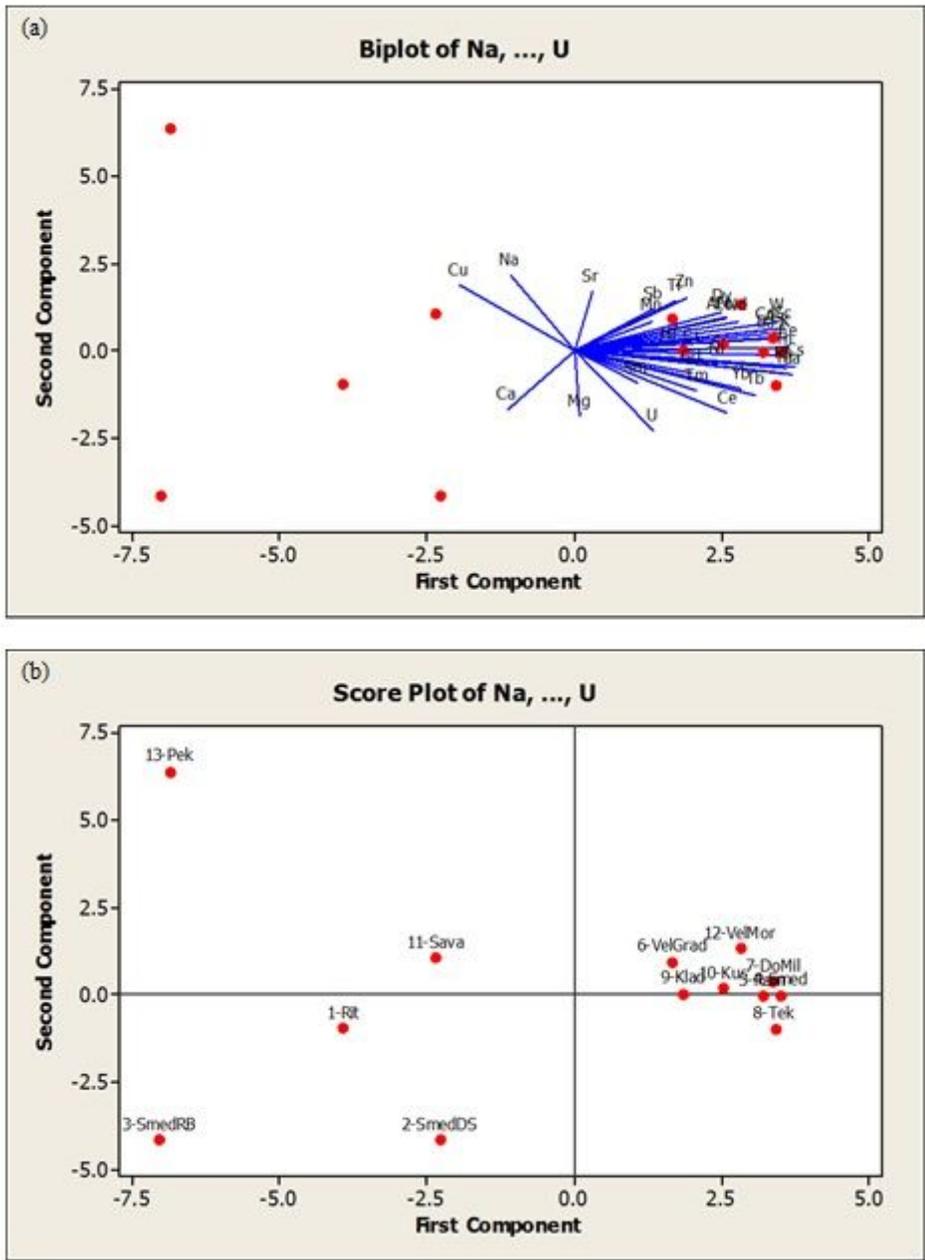


Figure 4

Score plot of PCA in analysis of total pool of results in regard to elements as (a) vectors, and (b) locations.

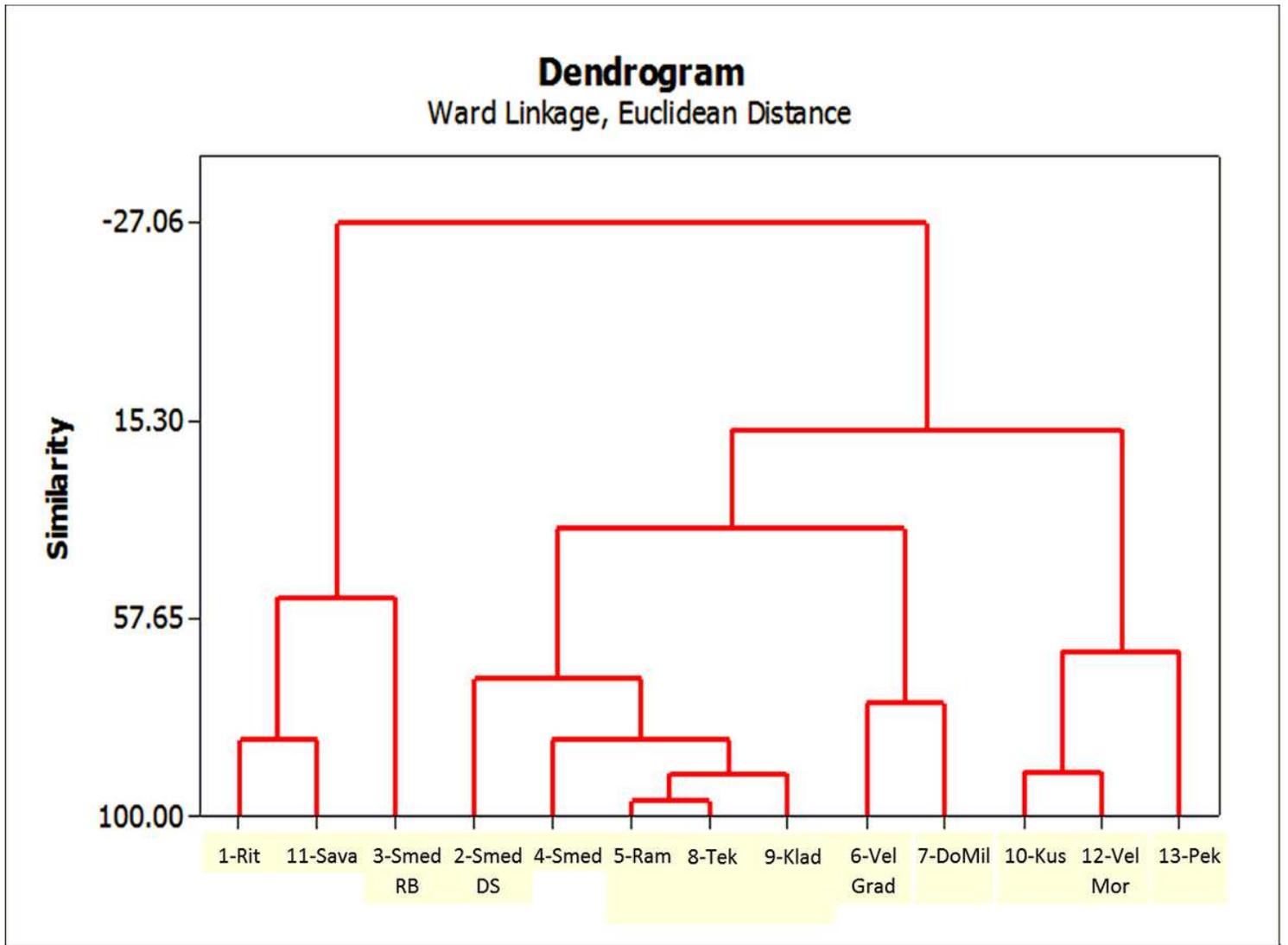


Figure 5

Dendrogram presenting hierarchical clustering of sampling locations. Analysis includes all determined elements.

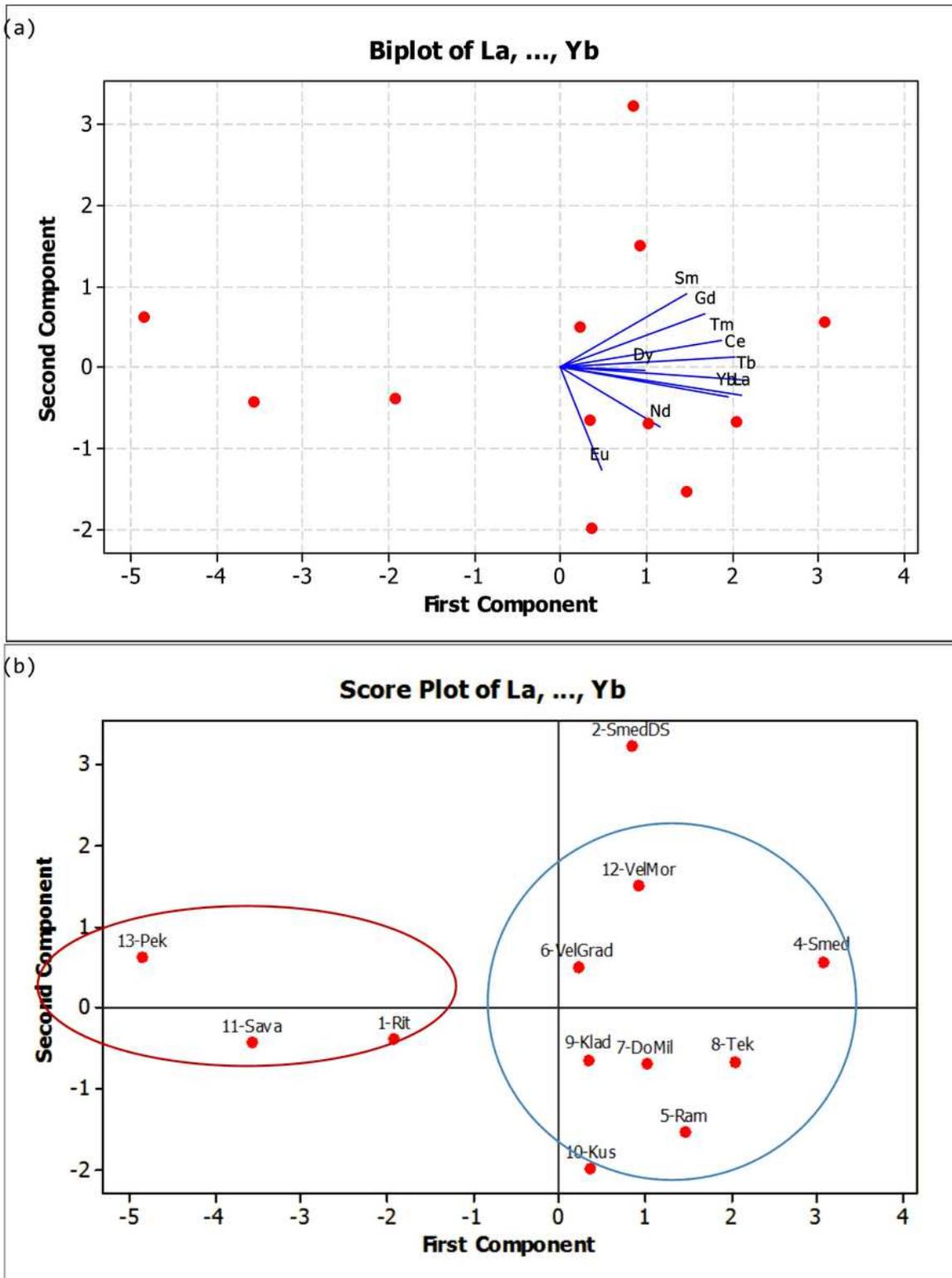


Figure 6

Score plot of PCA of relative concentrations of lanthanides in regard to elements as (a) variables, and (b) locations as objects.

Supplementary Files

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