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Geochemical hunting of lithogenic and anthropogenic impacts on polymetallic distribution (Bregalnica river basin, Republic of Macedonia)

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ABSTRACT

The main subject of this investigation was the assessment of the lithogenic and anthropogenic distribution of 69 elements in the sediments and fluvisol in the Bregalnica river basin. Alluvial soil and fluvisol samples were collected from the total of eighteen locations along the course of the Bregalnica river and additional thirteen samples were collected from its tributaries. The matrix elements accumulation patterns followed the order: Fe > Na > Al > Ca > Mg > K > Ti > P. The potentially toxic elements, such as As, Cd, Pb, and Zn, have enriched content in the sediments in the medium course of the river, where the main anthropogenic introduction activities occurred. By multivariate analysis the dominant geochemical associations were extracted, as follows: F1: Y-Eu-Lu-Cr-V-La-Gd-Nb-Co-Hf-Zr-Ga-Mg-Fe-Sr-Ta-Sn-Li-Na-Rb-Ni-Ge-Be-Cs; F2: As-W-Ba-Ag-Cu-Tl-Zn-Sb-Mo-In-Cd-Te-Bi-Pb and F3: I-Sc-Br-K. Lead and zinc contents were strongly correlated with the hydrothermal exploitations, especially in the area of Neogene clastite and vulcanite. These elements occur as dominant geochemical markers of the anthropogenic impacts of polymetallic enrichments due to the hydrothermal ore exploitation (Factor 2). The impact of Oligocene volcanism (Kratovo-Zletovo region) was observed in the lithological enrichments of Pb, Zn, Cu, As, Sb, Mo and Bi. Despite the natural distribution along the course of the Bregalnica river, an exceptional anomaly in the iron distribution of the old polymetallic unused mineralization was detected in Zone 1 (Berovo region).

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KEYWORDS
Alluvial soil; metals; pollution; multivariate analysis; spatial distribution

Introduction

Alluvial soils have been used as an important tool to assess the health status of aquatic ecosystems and represent an integral component of ecological integrity.[1–4] Sediments act as a sink of inorganic pollutants (potentially toxic elements/metals) and provide a history of anthropogenic pollutant input.[5] Toxic metals pollution in sediments has been proved to be an increasingly global problem, which is considered to pose a serious threat to the aquatic environment resulting from their toxicity, non-biodegradable and persistent nature, and the bio-enrichment ability in food chain.[4,6–9] These elements are deposited onto sediment surfaces and immobilized through adsorption, coagulation or flocculation and incorporation into the lattice structure of minerals and precipitation by forming insoluble fractionation.[4,10,11] Only a small portion of free metal ions, however, stay dissolved in water.[12] Thus, the distribution of trace metals in sediment adjacent to populated areas (includes industries, mining exploitation in particular) can give us the evidence of anthropogenic influence on aquatic system and convenience in assessing the potential risks associated with human waste discharge.[13] For example, in the Republic of Macedonia there are several significant pollution sources of potentially toxic elements/metals that continuously introduce tailings and waste into river waters.[14] These hotspots are predominantly present in the southeast part of the country. On the other hand, this region is characterized by a dominance of very old geological units specific for the Balkans area and even Europe as a whole. Regarding the dominance of the volcanic geological units and Pb-Zn mineral deposits, the region of the Bregalnica river basin is a specific region to monitor the geochemical interactions in various alluvial soils.[14,15] This region is characterized by several significant pollution sources of potentially toxic metals and other chemical elements in the environment: the copper mine and flotation *Bučim* near Radoviš and the Pb-Zn mines *Sasa* near Makedonska Kamenica and *Zletovo* near Probištip.[16] The excavation of the copper minerals is carried out from an open ore pit, while in the lead-zinc mines the exploitation is underground, and the ore tailings are stored outdoors. The ore produced in the mines is processed in the flotation plants, and in the process of flotation of the relevant minerals, flotation tailings are separated and disposed on a dumpsite in the open air.

The spatial hunting of dominant elements associations in the Bregalnica river basin represents the first attempt of this type in this unique area. The presence of dominant Oligocene volcanism in the area of the *Sasa* mine (Pb-Zn hydrothermal exploitation), the Kratovo-Zletovo district and in the area of the *Bučim* mine (Cu-Au hydrothermal exploitation) creates specific

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environmental conditions leading to lithogenic and anthropogenic poly-metallic enrichments. Therefore, the main objective of this study was to assess the lithogenic and anthropogenic distribution of a total of 69 elements along the Bregalnica river basin.

Multivariate statistical approach was implemented for hunting the dominant geochemical associations. Alluvial soil samples (sediment and fluvisol) were collected for the historical record of the lithological and anthropological impact on the elements' geochemistry. The dominant lithogenic and anthropogenic markers were extracted and the spatial pattern of each geochemical marker was generated.

Materials and methods

Investigated area

The investigated area includes the basin of the river Bregalnica, which is located in the east planning region of the Republic of Macedonia. The area of the Bregalnica river basin covers ~200 km (W-E) × 200 km (S-N) within the following geographic coordinates N: 41°27′–42°09′ and E: 22°55′–23°01′ (Fig. 1). The region of the investigated area is geographically composed of several sub-regions. These sub-regions are characterized by specific generalized geology and land use. As a consequence of the industrialization, urbanization and lack of treatment of the wastewaters from the industry, the mines and the city sewerage, the waters of this important hydrographic factor are exposed to a high level of pollution, from the aspect of introduction of higher contents of certain toxic metals. The pollution is frequently particularly high at low river flows, as in the case of the river Bregalnica in its course through the Kočani valley (central part of the investigated area). The east and north parts of the investigated area are mainly mountainous parts while the central and western parts consist of cultivated agricultural land (Fig. 2).

The precipitation is mostly related to and conditioned by the Mediterranean cyclones. During the summer period, the region

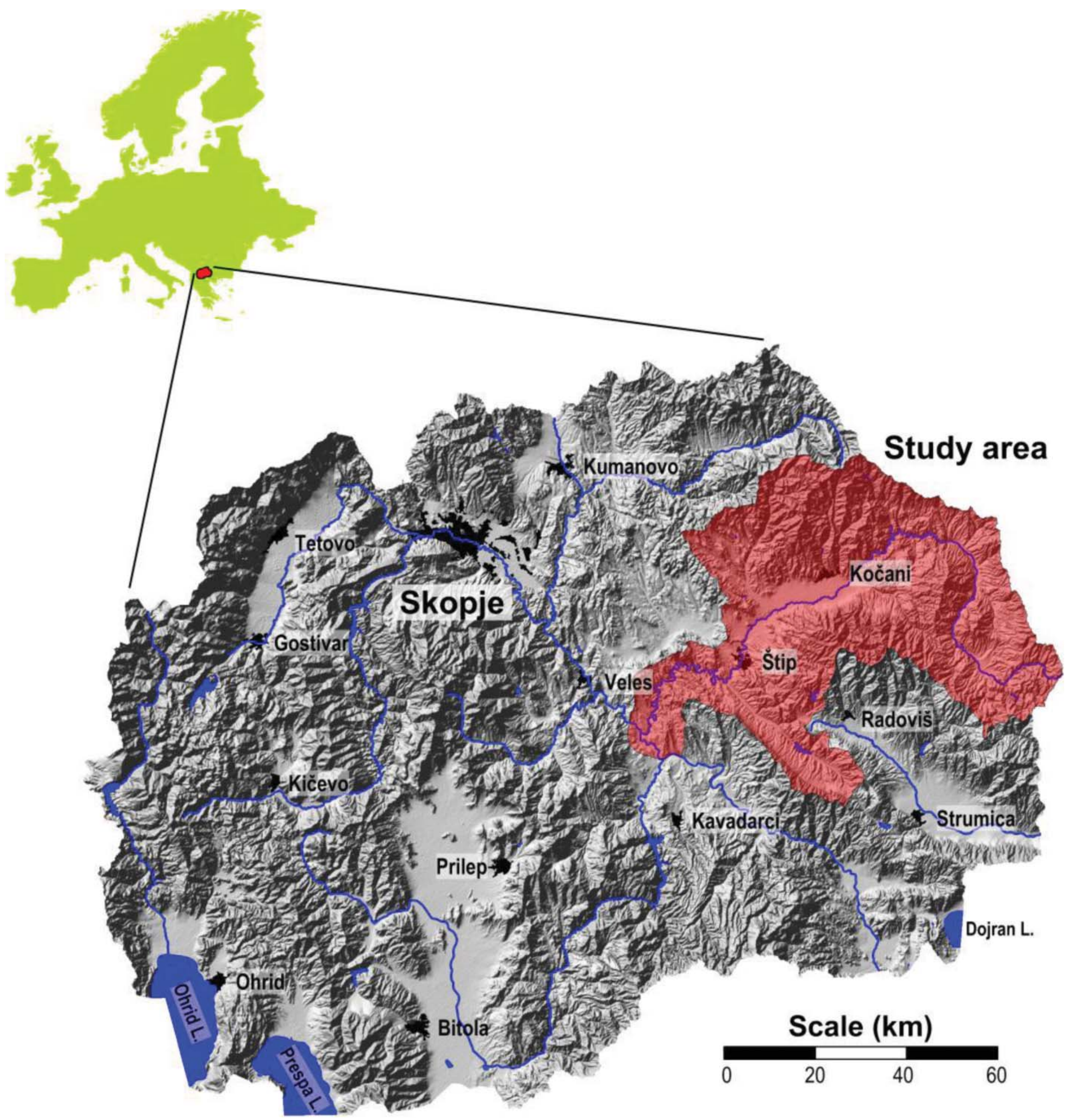

Figure 1. The investigated area on the territory of the Republic of Macedonia.

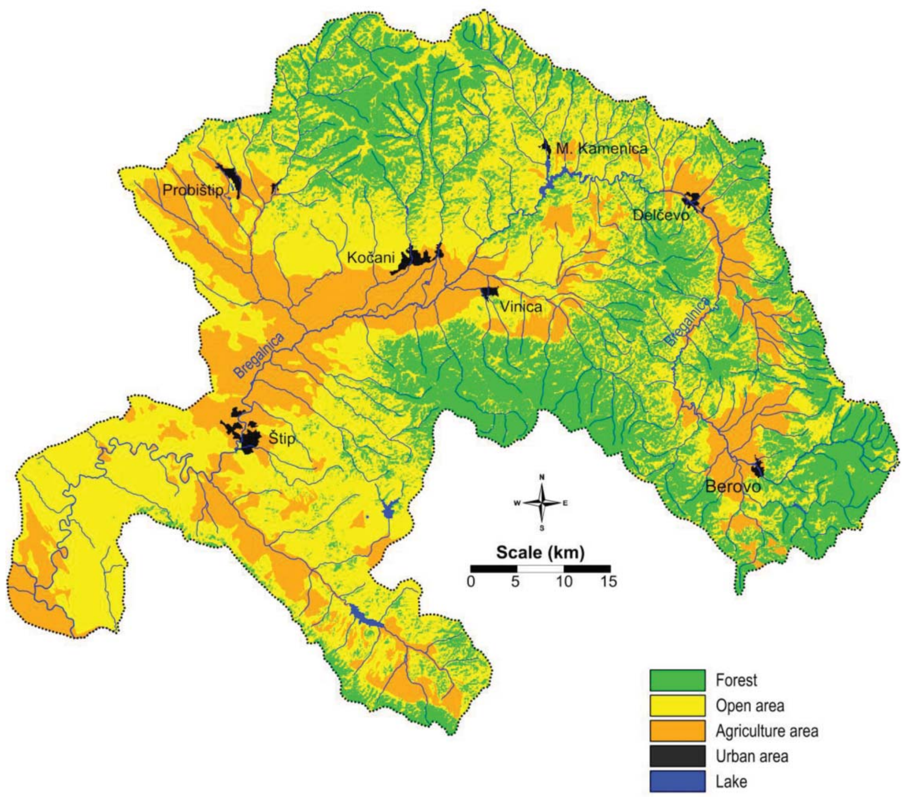

Figure 2. The region of the investigated area including the type of land use.

is most often found in the centre of the subtropical anticyclone, which causes warm and dry summers. From the central area of the region, as the driest area, the average annual precipitation increases in all directions, because of the increase either in the influence of the Mediterranean climate or the increase in altitude. As regards the total annual number of sunny hours, there are about 6 h per day in this area. In the region are distinguished about ten climatic-vegetation soil areas with considerably heterogeneous climate, soil and vegetation characteristics.[17]

Generalized geology and dominant ore mineralization of the investigated area

Southeast Europe has undergone a complex Alpine tectonic evolution. The Srednogorie zone, Kraishte and the Rhodope Massif in Serbia, Macedonia and Bulgaria were sites of extensive westward/southward younging magmatic activity, starting in the Jurassic and up to the Cretaceous period, with the closure of the Vardar zone.[18,19] The investigated area that covers the basin of the river Bregalnica lies on two main tectonic units: the Serbian-Macedonian massive and the Vardar zone.[19] The polyphasic Neogene deformations associated with the volcanic activities through the insignificant movements had direct influence on the gradual formation of the reefs and the formation of deposits in the existing basins (Fig. 3). From the middle Miocene to the end of the Pleistocene there were alternating periods of fast and slow landslide accompanied with variable sedimentation (deposition).

The Cenozoic volcanism represents a more recent extension in the Serbian-Macedonian massive and the Vardar zone. The oldest volcanic rocks can be found in the areas of Bučim, Damjan, the Borov Dol district and in the zone of Toranica, Sasa, Delčevo and Pehčevo.[18] These older volcanic rocks were formed in the mid Miocene from sedimentary rocks that represent the upper age limit of the rocks. The origin of these oldest volcanic rocks is related to the Oligocene – the early Miocene period. The following are categorized as volcanic rocks: andesite, latite, quartz-latite and dacite. Volcanism appears sequentially and in several phases forming sub-volcanic areas. On the other hand, the pyroclastites are most frequently found in the Kratovo-Zletovo volcanic area, where the dacites and andesites are the oldest formations. Generalized geology of the area is generated based on the data provided by Rakićević et al. and presented in Figure 3.[20] The most important Macedonian metal deposits are related to the regional magmatic activity that occurred in the southern parts of the Carpato-Balkanides during the Eocene-Pliocene.[21,22] The *Zletovo mine* is located near the town of Probištip. As presented by Serafimovski et al. the mineralization of this deposit is related to the Tertiary calc-alkaline magmatic rocks (dacites and andesites) and it is found in a dacitic volcano-sedimentary suite that had been altered to clays and micas.[21] The *Sasa mine* is situated near the city of Kamenica. The mineralization is located along the contact line between the Miocene calc-alkaline igneous bodies (latites and dacites) and the graphite-chlorite-sericite shists, gneisses and limestones.[23] The ore consists of pyrite, galena and sphalerite with additional magnetite and chalcopyrite, while the mass fractions of Pb and Zn are around 10% with additional contents of Ag, As, Cd, Mn and Sb. The ore is concentrated at the mine by flotation and the tailings are stored in a dam in the valley just below the

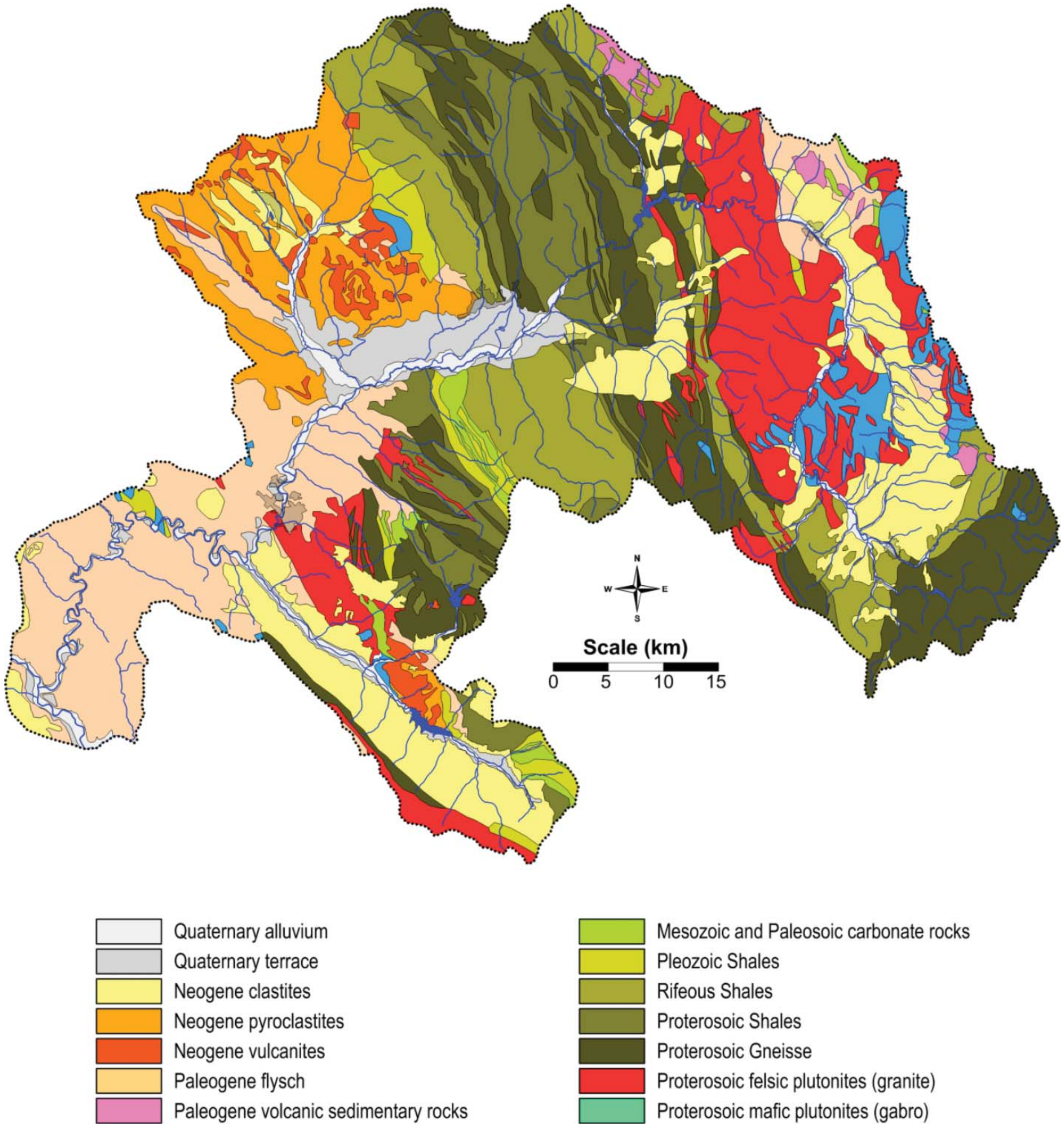

Figure 3. Generalized geology of the whole investigated area.

mine. The Kamenička River is culverted beneath the tailings dam and flows for 12 km until it meets in the Kalimanci Lake (artificial reservoir on the Bregalnica River). The *Bucim mine* is situated near the town of Radoviš. Copper-porphyry type of mineralization occurs in this deposit.[23,24] The ore concentrate is characterized by average content of 0.3% Cu and 0.3 g/t Au.[25] The milling and flotation plants discharge their drainage waters in the river Lakavica.

Sampling strategy and protocols

In the period August-November 2012, samples of river sediments and fluvisol were collected, as well as natural and anthropogenic alluvium from the river plains along the course of the river Bregalnica, in accordance with a previously specified sampling network. Apart from the above-mentioned locations for sample collection along the river course, some of the more important tributaries to the river Bregalnica were also additionally included in the location network, in order to determine the influence of the potentially polluted waters from the tributaries on the pollution of the main hydrographic factor. The more important tributaries of the river Bregalnica that were included in the sample network were the following: Ratevska River, Očipalska River, Kamenička River, Kočanska River, Orizarska River, Zletovska River, the river Lakavica and Ovčepolska River. Samples of water and river sediment were also collected from the river Vardar in the area where the river Bregalnica flows into the river Vardar.

The total basin area of the river Bregalnica was divided into four zones: zone 1 (Z-1) which includes 5 locations (B1, B2, B3, B4, and P1), zone 2 (Z-2), which includes the following 5 locations: B5, B6, B7, B8 and P2, zone 3 (Z-3) which includes the following 5 locations: B9, B10, B11, B12, and B13 and zone 4 (Z-4) which includes the following locations: B14, B15, B16, B17 and B18. The areas of the Kamenička River (K), Zletovska River (Z) and the river

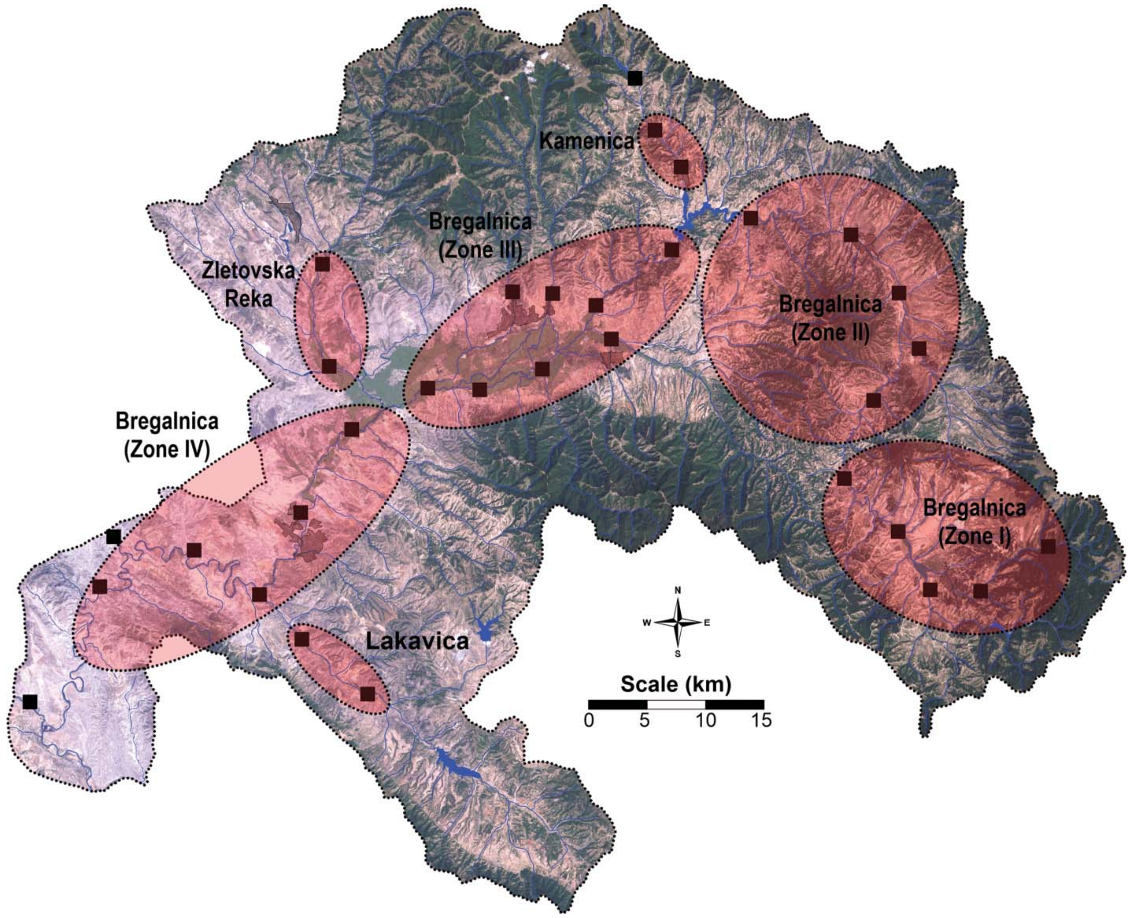

Figure 4. Locations for taking samples of water and sediment along the course of the river Bregalnica.

Lakavica (L) were separately monitored (Fig. 4). According to the previously set of sampling strategy, at each location sediment samples were collected using the following protocol: Fine grained sediment (0.06–2.0 mm) were carefully collected from the top two to four centimeters as a surface sediment composite sample (2–3 spots from one side of the river). Sediment was collected from beneath an aqueous layer directly, using plastic shovel. Following collection, sediment was transferred from the sampling device to a sample container for the analyses requested. Multiple grabs were placed into a container constructed of inert material, compositing representative sample. At the same location, wherefrom the sediments were collected, fluvisol samples were also collected from the alluvial terraces. The top layer (0–5 cm) of fluvisol was collected using plastic shovel. The representative sample was constructed collecting the fluvisol from the corners of 1 meter square.

Along the whole course of the river Bregalnica a total of 18 samples of sediments were collected. Additionally, samples were also collected from another 13 locations along the tributaries to the Bregalnica. The locations wherefrom the samples were collected are presented in Figure 4. The geographic coordinates of each location were also determined to enable mapping of the generated information about the values of the contents of the investigated elements. This step is nevertheless required for the monitoring of the distribution of the investigated elements along the course of the river Bregalnica.

Sample physical-chemical pre-treatment

The preparation of the collected samples for the analysis of the 69 elements was carried out by their cleaning, drying, breaking and digestion. For digestion of the samples of alluvial soil the method of open digestion with mixture of mineral concentrated acids was applied. The samples brought in the laboratory were subjected to cleaning and homogenization, drying at room temperature, or in a drying room at 40°C, to a constantly dry mass. Then the samples were passed through a 2-mm sieve and finally were homogenized by grinding in a porcelain mortar until reaching a final size of the particles of 25 μm. Following the physical preparation, the samples were chemically prepared by wet digestion, applying a mixture of acids in accordance with the international standard.[26] Precisely measured mass of sample (0.25 g) was placed in Teflon vessels and 5 mL concentrated nitric acid (HNO_3, 69%, wt v^{-1}, trace select purity, Merck, Munich, Germany) was added, until the brown vapors came out of the vessels, on reaching a temperature of 180°C. For total digestion of inorganic components, 5–10 mL of hydrofluoric acid (HF, $\geq$40%, wt v^{-1}p.a. Merck, Munich, Germany) was added. When the digest became a clear solution, 2 mL of perchloric acid ($HClO_4$, p.a. purity, Alkaloid, Skopje, Macedonia) was added for total digestion of the organic compounds. After cooling the vessels for 15 min, 2 mL of hydrochloric acid (HCl, 37%, t, wt v^{-1}, trace select purity, Merck, Munich, Germany) and 5 mL of double ionized water were added for dissolving of metal ions totally. Finally, the digest was transferred into the 25 mL volumetric flasks. Thus, the digested alluvial soil samples were prepared for determination of the contents of the different elements by applying atomic emission and mass spectrometry.

Instrumentation and determination of the elements content

SCIEX Perkin Elmer Elan DRC II (Canada) inductively coupled plasma mass spectrometer (quadrupole as single detector) was used for measurement of the concentration of the trace elements. All measurements were carried out using the semiquantitative method (Total Quant) supplied by Elan 3.4 software that uses a response factor calibration curve, which was obtained by calibration in multiple points, low, medium, and high concentration, for optimum setup, using a multielement Merck VI standard solution, diluted to mimic the real sample consumption. Atomic emission spectrometer with inductively coupled plasma, ICP-AES, (model 715ES, Varian, Palo Alto, CA, USA), was used for measurement of the concentration of several elements (Al, Ca, Fe, K, Mg, Na and P). For each element analyzed, previous optimization of the instrumental conditions was performed. The instrumental and operating conditions for each of the above-mentioned techniques are presented in Table 1. In all samples, the contents of a total of 69 elements were analyzed: Ag, As, Al, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Ti, Th, Tl, Tm, V, W, Y, Yb, Zn and Zr.

The limits of detection (LOD) were based on the usual definition as the concentration of the analytic yielding a signal equivalent to three times the standard deviation of the blank signal, using 10 measurements of the blank for this calculation. The calculated values for the detection limits are presented in Table 2. Both certified reference materials (NIST-SRM 2711a, Montana II Soil, National Institute of Standards & Technologies, Gaithersburg, MD, USA) and spiked intra-laboratory

Table 1. Instrumental conditions for ICP-MS and ICP-AES.

RF Generator	ICP-AES	ICP-MS
Power output of RF generator	1500 W	
Power output stability	Better than 0.1%	
ICP Ar flow gas rate	15 L min^{-1}	
Plasma parameters		
Nebulizer	V- groove	Micromist
Spray chamber	Double-pass cyclone	
Peristaltic pump	0–50 rpm	
Cones	/	Platinum
Plasma configuration	Radially viewed	Axially viewed
Spectrometer	Echelle optical design	Quadrupole
Polychromator	400 mm focal length	/
Polychromator purge	0.5 L min^{-1}	/
Total voltage/V	/	0.1
Integration measurement time/ms	/	0.1
Measurement at one point (isotope)/s	/	300
Repetitions measurement	3 per point	
Conditions for program		
ICP-AES measurements	ICP-MS measurements	
Element	Wavelength, nm	Isotopes
Al	396.152	107Ag, 75As, 27Al, 197Au, 11B, 137Ba, 9Be, 209Bi, 79Br, 114Cd, 140Ce, 59Co, 53Cr, 133Cs, 63Cu, 163Dy, 166Er, 153Eu, 56/57Fe, 69Ga, 157Gd, 72Ge, 178Hf, 201/202Hg, 165Ho, 127I, 115In, 193Ir, 139La, 7Li, 175Lu, 55Mn, 95Mo, 93Nb, 146Nd, 60Ni, 189Os, 206/207/208Pb, 105Pd, 141Pr, 195Pt, 85Rb, 185Re, 103Rh, 101Ru, 121Sb, 45Sc, 77Se, 147Sm, 120Sn, 88Sr, 181Ta, 159Tb, 125Te, 47Ti, 232Th, 205Tl, 169Tm, 51V, 182W, 89Y, 172Yb, 66Zn, 90Zr
Ca	370.602	
Fe	238.204	
Mg	280.270	
K	766.491	
Na	589.592	
P	213.618	

Table 2. Lower detection limit for the analyzed elements.

Element	Unit	LOD[a]	Element	Unit	LOD[a]
Ag	mg/kg	0.01	Mn	mg/kg	0.01
Al	%	0.9	Mo	mg/kg	0.01
As	mg/kg	0.1	Na	%	0.1
Au	mg/kg	0.01	Nb	mg/kg	0.1
B	mg/kg	0.01	Nd	mg/kg	0.01
Ba	mg/kg	0.01	Ni	mg/kg	0.01
Be	mg/kg	0.01	Os	µg/kg	0.1
Bi	mg/kg	0.01	P	mg/kg	10
Br	mg/kg	0.01	Pb	mg/kg	0.01
Ca	%	10	Pd	mg/kg	0.1
Cd	mg/kg	0.01	Pr	mg/kg	0.01
Ce	mg/kg	0.05	Pt	mg/kg	0.01
Co	mg/kg	0.001	Rb	mg/kg	0.1
Cr	mg/kg	0.001	Re	mg/kg	0.01
Cs	mg/kg	0.01	Rh	mg/kg	0.01
Cu	mg/kg	0.01	Ru	µg/kg	0.1
Dy	mg/kg	0.01	Sb	mg/kg	0.01
Er	mg/kg	0.01	Sc	mg/kg	0.1
Eu	mg/kg	0.01	Sm	mg/kg	0.1
Fe	%	0.01	Sn	mg/kg	0.01
Ga	mg/kg	0.01	Sr	mg/kg	0.01
Gd	mg/kg	0.01	Ta	mg/kg	0.1
Ge	mg/kg	0.01	Tb	mg/kg	0.01
Hf	mg/kg	0.01	Te	µg/kg	0.01
Hg	mg/kg	0.01	Th	µg/kg	0.1
Ho	mg/kg	0.01	Ti	%	0.1
I	mg/kg	0.01	Tl	mg/kg	0.1
In	µg/kg	0.01	Tm	mg/kg	0.01
Ir	µg/kg	0.01	V	mg/kg	0.01
K	%	0.01	W	mg/kg	0.01
La	mg/kg	0.01	Y	mg/kg	0.01
Li	mg/kg	0.01	Yb	mg/kg	0.01
Lu	mg/kg	0.01	Zn	mg/kg	0.01
Mg	%	0.1	Zr	mg/kg	0.01

[a]LOD-limit of detection.

samples were analyzed at a combined frequency of 20% of the samples. The recovery for all of the analyzed elements ranges from 76.8% for Tl to 119% for Sb (for ICP-MS measurements) and from 87.5% for Na to 112% for P (for ICP-AES measurements).

Data processing

The data for the contents of the investigated elements were statistically processed using statistical software (Stat Soft, 11.0, Dell Software, Aliso Viejo, CA, USA) and conducting parametric and non-parametric analysis. Basic descriptive statistical analysis was conducted on the values of the contents of the elements in all types of samples. At the same time, normalization tests were conducted and based on the obtained results and the visual check of distribution histograms, the distribution of the data for the independent variables (elements' contents) was determined. For data normalization, the method of *Box-Cox* transformation was also applied.[27] The F-test was applied for processing of certain data for the needs of comparative analysis. Factor analysis (FA) and cluster analysis (CA) were used as methods for multivariate analysis.[28] In the preparation of the distribution maps the Kriging method with linear variogram interpolation was applied. Percentile values of the distribution of the interpolated values were considered as area limits.[29]

Results and discussion

Lithogenic and anthropogenic distribution in sediment and fluvisol

The complete overview of the elements' contents, i.e. the values of the medians in the sediments and alluvial soils, is presented

Table 3. Descriptive statistics for the values of elements' contents in samples of alluvial soil (N = 32, for the whole basin).

		Sediment					Fluvisol				
Element	Unit	Min	P_{25}	Median	P_{75}	Max	Min	P_{25}	Median	P_{75}	Max
Al	%	3.3	5.8	6.1	6.4	7.3	4.8	5.6	6.1	6.5	6.9
Ca	%	0.67	1.7	1.9	2.6	5.4	0.97	1.4	1.8	2.2	4.0
Fe	%	1.3	5.0	6.2	7.4	39	0.92	2.5	3.3	4.6	24
K	%	0.028	0.082	0.29	0.49	1.4	0.018	0.069	0.32	0.89	1.4
Mg	%	0.54	0.87	1.0	1.4	4.7	0.25	0.44	0.63	0.85	5.0
Na	%	0.69	1.6	3.2	5.3	18	0.62	1.2	1.7	4.0	13
P	%	0.056	0.083	0.10	0.11	0.35	0.032	0.057	0.073	0.086	0.33
Ti	%	0.071	0.26	0.50	0.62	0.93	0.053	0.13	0.24	0.33	0.65
Ag	mg/kg	0.34	0.82	1.0	1.5	4.6	0.27	0.35	0.72	1.1	2.9
As	mg/kg	7.9	14	18	28	140	5.3	7.9	13	21	130
B	mg/kg	0.071	20	33	42	86	0.005	0.005	0.41	1.0	8.9
Ba	mg/kg	240	470	630	780	2100	240	340	470	580	2300
Be	mg/kg	0.65	1.6	2.1	3.0	5.3	0.58	0.95	1.6	1.8	4.7
Bi	mg/kg	0.005	0.15	0.25	0.39	19	0.005	0.032	0.065	0.22	2.5
Br	mg/kg	0.005	0.005	1.1	2.9	6.6	0.005	0.005	1.1	1.7	5.4
Cd	mg/kg	0.062	0.24	0.35	1.1	22	0.005	0.051	0.11	0.44	3.5
Co	mg/kg	5.6	11	15	23	52	4.2	5.9	7.6	12	40
Cr	mg/kg	24	57	74	100	180	17	25	41	52	170
Cs	mg/kg	1.4	2.3	3.2	4.6	20	0.26	1.2	1.9	2.6	18
Cu	mg/kg	20	36	51	99	430	7.6	15	28	54	180
Ga	mg/kg	6.6	16	25	32	72	4.9	7.5	12	16	50
Ge	mg/kg	0.005	1.1	1.4	1.7	3.8	0.005	0.24	0.51	0.73	3.1
Hf	mg/kg	0.31	0.77	1.0	1.6	3.9	0.22	0.34	0.63	0.83	3.0
I	mg/kg	0.005	0.089	0.23	0.47	0.98	0.005	0.005	0.032	0.061	0.13
In	µg/kg	5.0	46	93	120	790	5.0	13	24	81	560
Li	mg/kg	10	17	32	47	82	3.7	12	15	22	76
Mn	mg/kg	340	1000	1600	3100	9900	340	440	650	1200	12000
Mo	mg/kg	0.042	0.61	0.95	1.5	5.2	0.005	0.20	0.41	0.93	4.5
Nb	mg/kg	4.1	8.5	13	18	31	2.8	4.4	6.5	7.8	19
Ni	mg/kg	12	20	32	41	93	3.4	9.3	14	20	54
Pb	mg/kg	18	25	32	68	11000	6.7	13	26	59	34000
Pd	mg/kg	0.050	0.24	0.77	1.9	6.4	0.050	0.12	0.20	0.48	4.5
Pt	µg/kg	95	180	230	270	600	5.0	9.4	20	92	210
Rb	mg/kg	30	56	82	120	230	16	43	52	64	290
Sb	mg/kg	0.21	0.32	0.46	1.0	4.6	0.13	0.21	0.43	0.72	6.4
Sc	mg/kg	1.6	5.4	13	17	23	0.90	2.9	7.8	13	21
Sn	mg/kg	0.005	3.5	4.7	6.0	15	0.41	1.2	1.7	2.1	5.6
Sr	mg/kg	98	170	230	310	1100	62	84	120	190	1200
Ta	mg/kg	0.36	0.80	1.2	1.6	2.9	0.25	0.45	0.61	0.80	2.3
Te	µg/kg	5.0	15	32	60	2000	5.0	9.3	21	49	420
Tl	mg/kg	0.13	0.35	0.48	0.70	2.7	0.050	0.21	0.30	0.43	4.5
V	mg/kg	53	97	150	210	910	37	51	74	100	500
W	mg/kg	0.73	1.2	1.5	2.2	10	0.20	0.68	0.90	1.3	3.5
Y	mg/kg	8.5	18	29	41	80	5.3	8.9	12	18	48
Zn	mg/kg	25	86	120	300	3400	10	30	55	140	930
Zr	mg/kg	8.9	24	34	49	130	6.3	10	19	26	110

P_{25}-25 percentile; P_{75}-75 percentile.

in Table 3. The contents of the macro, micro and elements in traces in the first place depend on the geochemical processes and hydrographic conditions, as well as on the mechanical structure of the alluvial soils, as stated by Du Laing et al.[10] Of all 69 analyzed elements, the contents of only five elements were not determined as their presence was below the detection limit (Au, Os, Re, Ru and Th). The basic, matrix elements (Al, Ca, Mg, K, Fe, Na, P and Ti) show significant stability with insignificant variations along the whole course of the river Bregalnica. The concentration of the major elements Na, K, Ca, and Mg was usually associated with the increase of the soil salinity.[8] The addition of Ca-salts usually results in a higher release of exchangeable metals in the soil solution compared to the addition of Na-salts, which are less competitive for

Table 4. T-test and F-test for the contents of the elements in the sediments of the different zones in the course of the Bregalnica river.

	Zone 1 vs. Zone 2				Zone 2 vs. Zone 3				Zone 3 vs. Zone 4			
Element	t	*P*	F	*P(var)*	T	*P*	F	*P(var)*	t	*P*	F	*P(var)*
Al	0.25	**0.80****	1.57	0.22	−1.35	**0.19***	1.25	0.75	−0.25	**0.80****	1.85	0.35
Ca	1.22	0.23*	1.82	0.10	0.83	0.41*	1.05	1.00	−0.71	0.49*	2.25	0.22
P	3.89	0.001	1.81	0.10	0.14	**0.89****	2.94	0.07	0.14	**0.89****	1.82	0.36
Ag	2.97	0.001	1.54	0.24	−0.11	**0.91****	4.30	0.02	0.24	**0.81****	1.70	0.42
As	2.33	0.02	1.90	0.08	3.12	0.001	1.52	0.49	−1.63	0.12*	1.06	0.93
B	10.6	0.001	1.74	0.13	0.30	**0.76****	1.39	0.60	0.07	**0.94****	1.58	0.48
Ba	2.15	0.04	1.09	0.82	0.70	0.49*	1.86	0.30	−0.25	**0.81****	1.24	0.74
Be	2.83	0.01	1.10	0.78	0.40	**0.69****	4.11	0.02	−0.83	0.42*	1.26	0.72
Bi	2.95	0.001	1.01	0.98	−0.30	**0.76****	2.65	0.11	0.25	**0.80****	1.83	0.35
Br	0.12	**0.90****	1.47	0.29	−0.70	0.49*	2.32	0.16	−0.42	**0.68****	1.99	0.29
Cd	3.14	0.001	1.59	0.20	−0.71	0.48*	3.13	0.06	0.12	**0.91****	2.28	0.21
Ce	5.13	0.001	1.31	0.46	1.55	0.13*	2.96	0.07	−1.07	0.30*	1.59	0.47
Co	4.64	0.001	1.60	0.20	2.03	0.05	2.19	0.19	−1.44	0.17*	1.61	0.46
Cr	5.04	0.001	1.38	0.38	1.25	**0.22***	1.40	0.59	−1.12	0.28*	1.33	0.66
Cs	3.55	0.001	1.97	0.06	0.21	**0.84****	9.15	0.00	−0.85	0.40*	2.08	0.26
Cu	3.99	0.001	2.16	0.04	2.46	0.02	4.45	0.02	−1.09	0.29*	1.73	0.40
Dy	5.03	0.001	1.17	0.67	1.36	**0.18***	2.60	0.11	−0.71	0.49*	1.38	0.62
Er	4.84	0.001	1.13	0.74	1.18	**0.25***	2.39	0.15	−0.51	**0.62****	1.15	0.83
Eu	5.15	0.001	1.23	0.56	2.38	0.02	2.33	0.16	−1.26	0.22*	1.41	0.60
Fe	3.21	0.001	1.16	0.69	2.39	0.02	11.95	0.00	−1.24	0.23*	4.62	0.02
Ga	4.18	0.001	1.00	1.00	1.39	**0.17***	2.36	0.15	−0.79	0.44*	1.66	0.44
Gd	5.34	0.001	1.24	0.56	1.50	**0.14***	2.82	0.09	−0.84	0.41*	1.60	0.47
Ge	4.63	0.001	1.07	0.85	−0.05	**0.96****	2.47	0.13	−0.12	**0.91****	1.82	0.36
Hf	3.79	0.001	1.47	0.29	0.62	**0.54***	5.70	0.01	−0.07	**0.94****	1.36	0.64
Ho	4.95	0.001	1.18	0.64	1.24	0.22*	2.84	0.08	−0.72	0.48*	1.35	0.65
I	5.26	0.001	2.08	0.05	−1.45	0.15*	2.09	0.22	0.22	**0.83****	1.72	0.41
In	2.46	0.02	1.01	0.99	−0.36	**0.72****	2.90	0.08	0.43	**0.67****	1.82	0.36
K	−0.90	**0.37***	1.74	0.13	−1.85	0.07*	1.63	0.42	0.50	**0.63****	1.69	0.42
La	5.44	0.001	1.42	0.33	1.50	0.14*	3.14	0.06	−0.93	0.37*	1.66	0.44
Li	4.27	0.001	1.38	0.37	0.20	**0.84****	11.57	0.00	−1.33	0.20*	2.79	0.12
Lu	4.86	0.001	1.09	0.80	1.20	0.24*	2.63	0.11	−0.54	0.59*	1.28	0.71
Mg	4.42	0.001	2.11	0.04	2.14	0.04	1.82	0.32	−1.01	0.32*	1.09	0.89
Mn	3.43	0.001	1.22	0.58	1.45	0.15*	1.67	0.39	−0.53	**0.60****	1.29	0.69
Mo	2.54	0.01	1.08	0.83	1.21	0.23*	2.03	0.24	−0.27	**0.79****	2.52	0.16
Na	2.05	0.04	1.17	0.66	3.19	0.001	3.80	0.03	−0.72	0.48*	1.03	0.97
Nb	5.11	0.001	1.03	0.93	1.34	0.19*	2.25	0.18	−0.23	**0.82****	1.46	0.56
Nd	5.28	0.001	1.30	0.48	1.70	0.10*	3.13	0.06	−0.97	0.34*	1.55	0.50
Ni	5.21	0.001	2.14	0.04	0.82	0.42*	1.15	0.86	−1.07	0.30*	1.41	0.60
Pb	1.77	0.08*	2.18	0.03	−0.51	**0.61****	1.71	0.37	0.18	**0.86****	1.07	0.92
Pd	2.65	0.01	1.69	0.15	−2.07	0.04*	1.66	0.40	0.66	0.51*	1.69	0.42
Pr	5.38	0.001	1.31	0.46	1.65	0.11*	3.19	0.06	−1.06	0.30*	1.62	0.46
Pt	9.01	0.001	8.42	0.00	2.34	0.02*	39.93	0.00	1.61	0.12*	6.21	0.01
Rb	3.34	0.001	1.42	0.34	1.17	0.25*	5.82	0.01	−1.07	0.30*	2.37	0.19
Sb	1.57	0.12*	1.38	0.38	0.24	**0.81****	4.07	0.02	−0.59	0.56*	1.78	0.38
Sc	2.42	0.02	1.00	1.00	−1.02	0.31*	1.03	0.88	−0.31	**0.76****	1.32	0.67
Sm	5.36	0.001	1.24	0.55	1.74	0.09*	2.74	0.09	−0.98	0.34*	1.40	0.61
Sn	4.78	0.001	4.80	0.00	1.52	0.14*	2.80	0.09	−1.33	0.20*	2.00	0.29
Sr	4.27	0.001	1.98	0.06	1.16	0.25*	2.16	0.20	−1.12	0.28*	1.41	0.60
Ta	4.38	0.001	1.49	0.27	1.78	0.08*	3.02	0.07	−0.25	**0.81****	1.10	0.88
Tb	5.28	0.001	1.23	0.57	1.38	0.18*	2.95	0.07	−0.81	0.43*	1.54	0.51
Te	1.28	0.20*	1.13	0.74	0.16	**0.87****	2.66	0.10	0.35	**0.73****	1.48	0.55
Ti	4.10	0.001	1.57	0.22	−0.31	**0.76****	1.11	0.91	−0.18	**0.86****	1.15	0.83
Tl	2.61	0.01	1.91	0.08	−0.08	**0.94****	5.14	0.01	−0.40	**0.69****	1.52	0.52
Tm	4.55	0.001	1.03	0.93	1.15	0.26*	2.73	0.10	−0.52	**0.61****	1.29	0.70
V	4.50	0.001	1.43	0.32	1.84	0.07*	2.11	0.21	−1.03	0.32*	1.17	0.81
W	4.24	0.001	1.69	0.15	0.78	0.44*	7.95	0.00	−0.34	**0.74****	1.78	0.38
Y	4.88	0.001	1.12	0.75	1.28	0.21*	3.11	0.06	−0.69	0.50*	1.64	0.45
Yb	4.65	0.001	1.04	0.92	1.13	0.26*	2.41	0.14	−0.45	**0.66****	1.22	0.76
Zn	3.17	0.001	1.76	0.12	−0.15	**0.88****	5.91	0.01	−0.19	**0.85****	1.40	0.61
Zr	3.74	0.001	1.50	0.27	0.53	**0.60****	6.79	0.00	0.09	**0.93****	1.89	0.33

T- t value (T–test), F- F value,*- Significant difference at the 0.10 level,**- Significant difference at the 0.05 level.

sorption.[12] The sediments are characterized with median value of Ca contents of 1.9% and 1.8% in fluvisol vs. 1.6% and 1.7% for Na contents respectively (Table 3). Aluminum is present in the highest concentration in the sediment (6.6%) of the fourth zone of the Bregalnica river course, with almost insignificant variations to 5.5% in the alluvium of the river Lakavica. Of all matrix geogenic elements, only iron shows a trend of variability of its median values in the sediment and the alluvial soils in the whole basin of the river Bregalnica. Iron is usually the most predominant element that generates sulphide precipitates. As Du Laing et al.[10] report, it is released from reducible minerals such as oxides/oxihydroxides within the sedimentary layers, where sulphate reduction occurs, which results in ferrous Fe. A major difference in the Fe contents between the sediment and the fluvisol (6.5 and 6.1%, respectively) was not detected in the upper course of the river, while in the second, third and fourth zone a trend of lower Fe content in the alluvium as opposed to the sediment was perceived (Table 3). The maximum iron content (29%) was detected in the sediment of the Zletovska River. Generally, Fe occurs in soluble forms in acid environment. When a neutral pH is approached, Fe can only exist in insoluble form with low redox potentials or as a soluble organic complex in oxic soils.[10] These authors also reported that the reduction of Fe^{3+} does not start before the complete depletion of all Mn^{4+}. The total manganese contents in the river Bregalnica alluvial soil ranges from 0.034 to 1.2%.

Copper was found in higher contents in the sediments of the investigated area, in certain zones along the Bregalnica river course. In accordance with the Dutch standards (http://www.contaminatedland.co.uk/std-guid/dutch-l.htm), the optimum contents of Cu range up to 36 mg/kg. As presented in Table 3, along the whole course of the Bregalnica River (Zones 1–4), the Kamenička River and the Zletovska River, the copper contents in the sediment exceed the optimal value in accordance with the previously mentioned standards, while in the sediment of the Kamenička River the Cu contents exceed the action value (190 mg/kg). The copper content in the sediment of the Kamenička River amounts to 290 mg/kg.

Regarding cadmium contents, it is found in the sediment in maximum content of 22 mg/kg, while in the fluvisol the content of this element is not higher than 3.5 mg/kg (Table 3). Taking into consideration the Dutch standards for Cd contents in sediment (optimum value 0.8 mg kg^{-1} and action value 12 mg/kg), there is a significant increase in Cd contents in the sediment in the third zone along the course of the river Bregalnica. On the other hand, in the sediment of the Kamenička River, a median value of 15 mg/kg (Table 3) was obtained.

The cobalt contents do not show any significant variations in the sediment of the Bregalnica basin, except for the fact that in zone 2 along the course of the river Bregalnica, a value at the upper limit of the optimum value in accordance with the Dutch standards (25 mg/kg) was obtained. Lead is also found in contents that point to environment pollution. Maximum Pb contents were detected in the sediment of the Kamenička River (1.1%), and in the alluvial soils, as high as up to 3.4%. These values point to the characteristic negative effect of the Pb-Zn ore processing in the ore and flotation plants of the *Sasa* mine. The optimum values for the Pb contents in sediment according to the Dutch standards amounts to 85 mg/kg, while the action value is 530 mg/kg. The Pb contents in the sediment in the three zones from the river source to the Zletovska river mouth do not exceed the relevant Dutch optimum values. Nevertheless, for the lead content in the sediment of the Kamenička River, a median of 7100 mg/kg was obtained, while for the Zletovska River a median of 670 mg/kg was obtained (Table 3). The sediment is a natural archive of a great number of chemical parameters, and especially of various chemical elements, with particular accent on the potentially toxic metals. Therefore, it can be said that the area around the *Sasa* mine, i.e. the Kamenička River is exposed to higher concentration of Pb, which exceed the relevant action values of Pb in relation to the Dutch standards (530 mg/kg). Similarly to the lead, the zinc contents in the sediment also show a comparable trend of deposition, owing to the intensive introduction of these elements related to the activities in the ore plants and the ore flotation processes in the *Sasa* and *Zletovo* mines. The zinc contents in the sediment exceed the optimum values in accordance with the Dutch standards (140 mg/kg) in zones 3 and 4 along the river Bregalnica, as well as in the sediment of the Kamenička (2200 mg/kg) and Zletovska River (1000 mg/kg). The zinc content has a maximum value of

Table 5. Matrix of factor loadings-factor analysis (FA) of the elements' contents in samples of sediment and fluvisol.

Element	F1	F2	F3	Communality
Y	**0.95**	0.19	0.10	94.2
Eu-Lu	**0.94**	0.20	0.12	92.8
Cr	**0.89**	0.13	0.18	84.7
V	**0.89**	0.37	0.12	94.4
La-Gd	**0.87**	0.38	0.09	91.6
Nb	**0.87**	0.32	0.19	89.2
Co	**0.87**	0.38	0.10	90.6
Hf	**0.85**	0.20	−0.05	77.1
Zr	**0.85**	0.23	0.01	77.5
Ga	**0.85**	0.42	0.19	93.6
Mg	**0.84**	0.29	−0.16	82.4
Fe	**0.81**	0.37	−0.32	89.6
Sr	**0.78**	0.33	0.11	73.3
Ta	**0.78**	0.21	0.17	67.9
Sn	**0.77**	0.39	−0.08	74.8
Li	**0.76**	0.42	0.18	78.3
Na	**0.74**	0.23	−0.30	69.9
Rb	**0.73**	0.50	0.20	82.2
Ni	**0.69**	0.21	0.19	56.3
Ge	**0.68**	0.50	0.34	83.3
Be	**0.66**	0.44	0.40	79.8
Cs	**0.64**	0.58	0.05	74.8
As	0.52	**0.67**	−0.12	74.0
W	0.52	**0.75**	−0.04	83.6
Ba	0.50	**0.64**	0.32	75.8
Ag	0.48	**0.75**	0.03	79.9
Cu	0.42	**0.65**	−0.01	60.8
Tl	0.39	**0.76**	0.24	78.6
Zn	0.36	**0.84**	−0.03	84.3
Sb	0.33	**0.80**	−0.08	75.5
Mo	0.31	**0.76**	0.25	73.0
In	0.29	**0.83**	0.23	83.0
Cd	0.22	**0.86**	0.09	79.3
Te	0.21	**0.83**	0.20	77.5
Bi	0.08	**0.84**	0.34	81.6
Pb	0.05	**0.89**	−0.05	79.4
I	0.49	0.22	**0.66**	72.3
Sc	0.38	0.19	**0.78**	79.4
Br	−0.01	0.02	**0.90**	81.5
K	−0.25	0.14	**0.90**	89.6
Total variability (%)	41.9	28.4	9.9	**80.2**
Eingene value	24.3	4.48	3.27	

Bolded values represent dominant factor loadings for each factor.

3400 mg/kg in the sediment of the Kamenička River and 930 mg/kg in the fluvisol.

Although the geographical distribution of the microelements in alluvial soils is closely related to the composition of the parent materials, the soils often exhibit less variation in micronutrient contents than their parent rocks. Soil-forming processes greatly influence the trace element distribution within the soil profile.[12] Significant variations were not detected in the contents of the other elements in traces in the sediment and in the fluvisol soils, as well as in relation to the Dutch standards for these elements. Considering the rest of the elements, the overview of the contents of microelements and elements in traces by zones is provided in Table 4.

Student T-tests and F-tests were used to determine the significant differences in the contents of each element among the zones along the course of the river Bregalnica (Table 4). The first two zones in the upper course of the river showed significant statistical difference only in relation to the following elements: Al, Ca, Br, K, Pb, Sb, and Te (Table 4). For the rest of the elements, there were insignificant distribution variations. This area (Zones 1 and 2) lithologically relies on dominance of the Quaternary alluvium. The second zone, in comparison with the third zone, which starts after the mouth of the Zletovska River, that is, after the Kalimanci hydro accumulation, showed significant differences for almost all of the analyzed elements, except for As, Co, Cu, Eu, Fe, Mg and Na (Table 4). Between zones 2 and 3 there is a separate lithological unit, which shows predominance of Proterosoic granite, shales and gneisses (Fig. 3). The comparison of all elements between the third and the fourth zone pointed to significant statistical differences in the contents of all the 69 elements analyzed.

The comparative analysis of the different zones in the area of the Bregalnica river basin showed that the whole basin cannot be defined as a single area. There are certain lithogenic and anthropogenic factors that condition the distribution of different chemical elements, which differs from the expected natural distribution. The environmental disaster that took place in the Kamenička River (2003) because of discharge of flotation tailings is clearly confirmed today by the high contents of lead and zinc in the sediment and in the alluvial soils. These high metal contents are introduced with the river water into the waters of the hydro accumulation Kalimanci, which serves as anthropogenic filter for the high contents of lead and zinc that can reach the waters of the river Bregalnica.

Multivariate assessment for the dominant geochemical association

Apart from the monitoring of the distribution of the different chemical elements, that is, establishing their contents in the sediment and in the hydromorphic soils on the river terraces, the correlations of the 69 analyzed elements were also statistically processed. For this reason, based on factor analysis, three synthetic geochemical associations of elements were singled out. The first two geochemical associations are dominant factors with variability of 41.9% and 28.4% out of the total variability of the factor analysis (Table 5). In order to confirm the

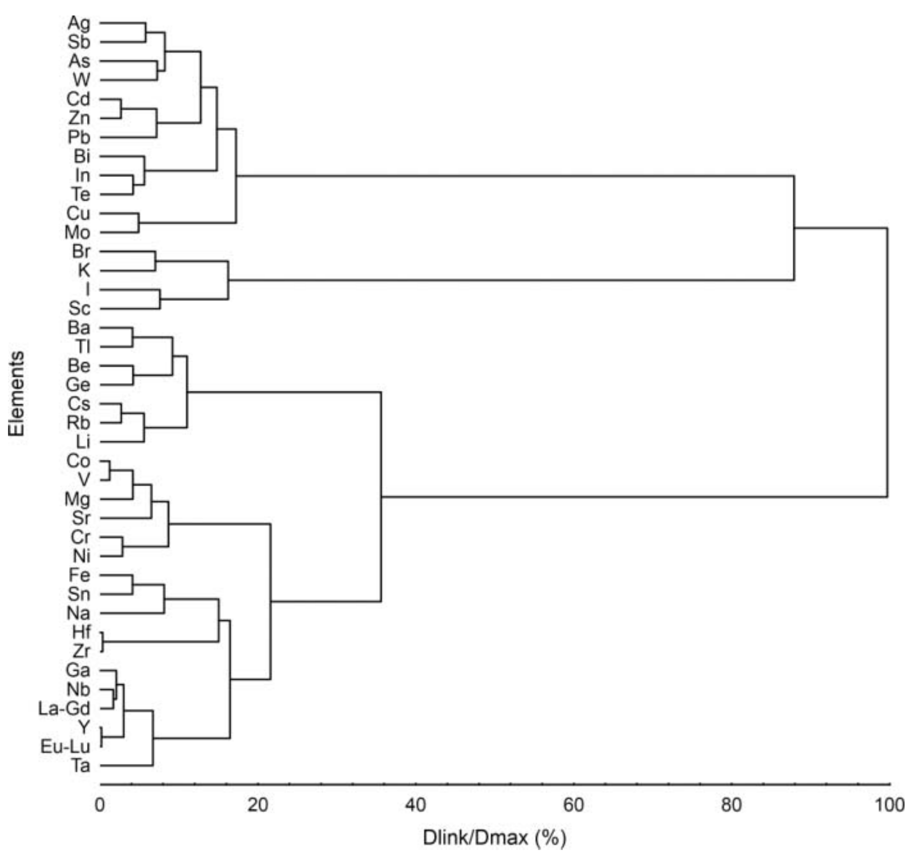

Figure 5. Dendrogram of dominant multivariate associations.

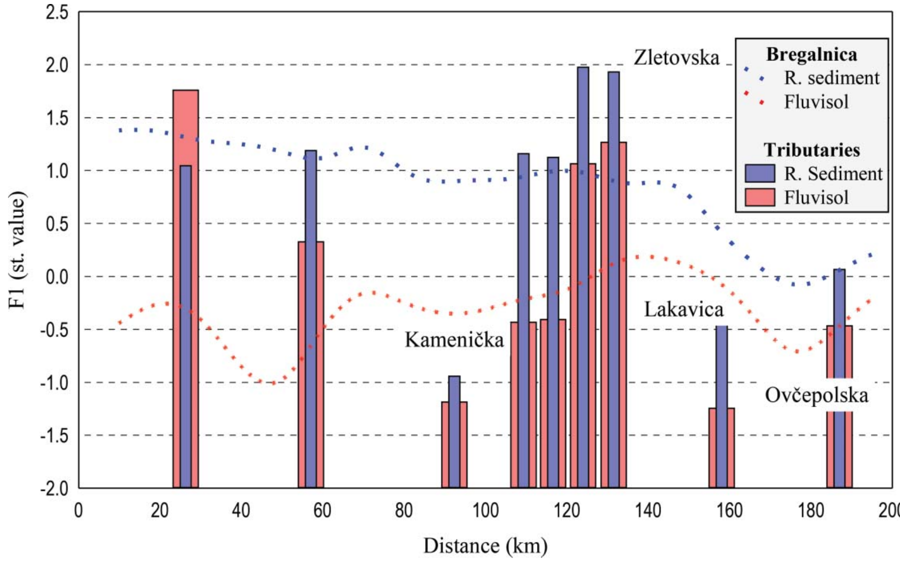

Figure 6. Distribution of F1 elements: Y-Eu-Lu-Cr-V-La-Gd-Nb-Co-Hf-Zr-Ga-Mg-Fe-Sr-Ta-Sn-Li-Na-Rb-Ni-Ge-Be-Cs in the sediment and the fluvisol soils in the course of the Bregalnica river and its tributaries. Tributaries: Ratevska River, Ochepalska River, Kamenička River, Osojnica, Orizarska River, Kočanska River, Zletovska River, Lakavica, Ovčepolska River.

inter-correlation of the elements contents, a cluster dendogram was also constructed (Fig. 5).

Factor 1 (F1) represents a natural geochemical association of the elements: Y-Eu-Lu-Cr-V-La-Gd-Nb-Co-Hf-Zr-Ga-Mg-Fe-Sr-Ta-Sn-Li-Na-Rb-Ni-Ge-Be-Cs. As a dominant factor with *Eingen*-value of significance of 24.3, it points to a stable distribution and strong correlation among these lithogenic elements. Their contents are due to the long-term deposition of the particles driven by the river water, that is, the particles created due to the earth erosion processes, rain-wash of rocks, particles carried by the wind etc. This dominant geochemical association is not subject to certain anthropogenic influences, which is also confirmed by the association of the rare earth elements (REEs) Eu-Lu and La-Gd. REE in terrigenous grains are largely unreactive and contribute an inherited signature.[30] The role of sediments as carriers and potential sources of REEs and metals is well established and a number of studies on the river basin and estuaries have yielded fundamental features of the aquatic geochemistry of the REEs.[30,31] Rare earth elements in the sedimentary rocks are mostly terrigenous and reveal the source rock composition reflecting the REE distribution in the exposed continental crust. These studies indicate that chemical-weathering reactions on the continent lead to extensive fractionation between the dissolved REEs and the river suspended particles and continental rocks.[15] Fractionation of REEs and metals occur predominantly in the solid phase during transport in the river systems. This geochemical association indicates very good stability in distribution along the whole course of the river.

Factor 2 (F2) is a geochemical association, which is processed based on the significant correlations among the elements: As, W, Ba, Ag, Cu, Tl, Zn, Sb, Mo, In, Cd, Te, Bi,

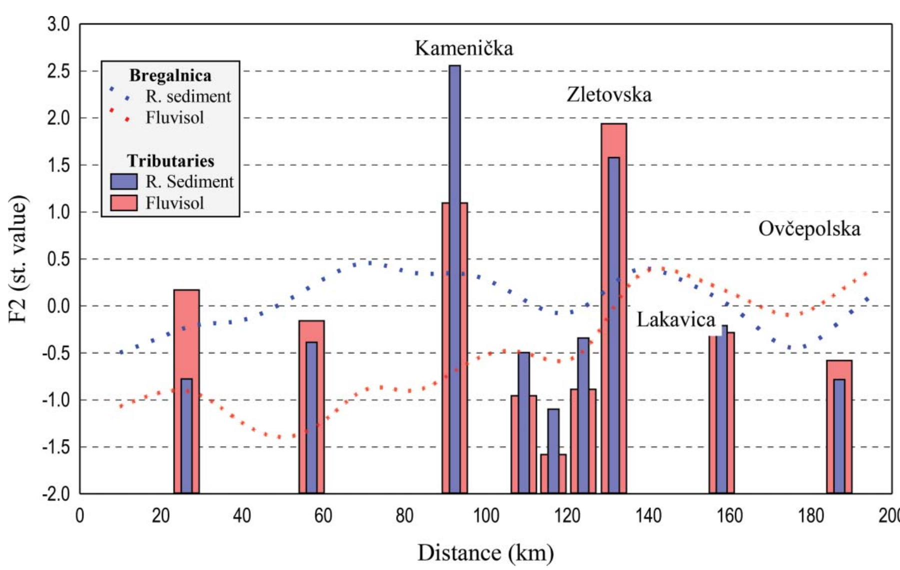

Figure 7. Distribution of F2 elements: As-W-Ba-Ag-Cu-Tl-Zn-Sb-Mo-In-Cd-Te-Bi-Pb in the sediment and the fluvisol soils in the course of the Bregalnica river and its tributaries. Tributaries: Ratevska River, Ochepalska River, Kamenička River, Osojnica, Orizarska River, Kočanska River, Zletovska River, Lakavica, Ovčepolska River.

and Pb. The contents of these elements are very frequently concentrated as a result of the processing of mineral raw materials. The association of Cd, Pb, Zn, Cu, Sb and Mo confirms this fact because the 90th percentile areas of the distribution of these elements associate in similar areas. An enhanced mobilisation of metals as dissolved organic complexes was observed for Pb, Cu and Zn [32] and for Cu and As, but not for Cd and Zn.[33] Charlatchka and Cambier found that Pb was especially complexed by organic acids in the alluvial soil.[34] The enrichment of these elements is dominant in Zone 3 where there is a significant use of the land for agricultural purposes. Application of technical measures leads to a significant increase in the organic mass in this area, and consequently to the increase in the mobility of As, Cu, Pb and Zn in this area.

Factor 3 (F3) is the least distinguished factor with variance of 9.9% out of the total variance and E-value of 3.3%. This geochemical association of elements is with non-specific characterization of distribution. The dominant elements are Br and K with values for factor loadings of 0.90. The

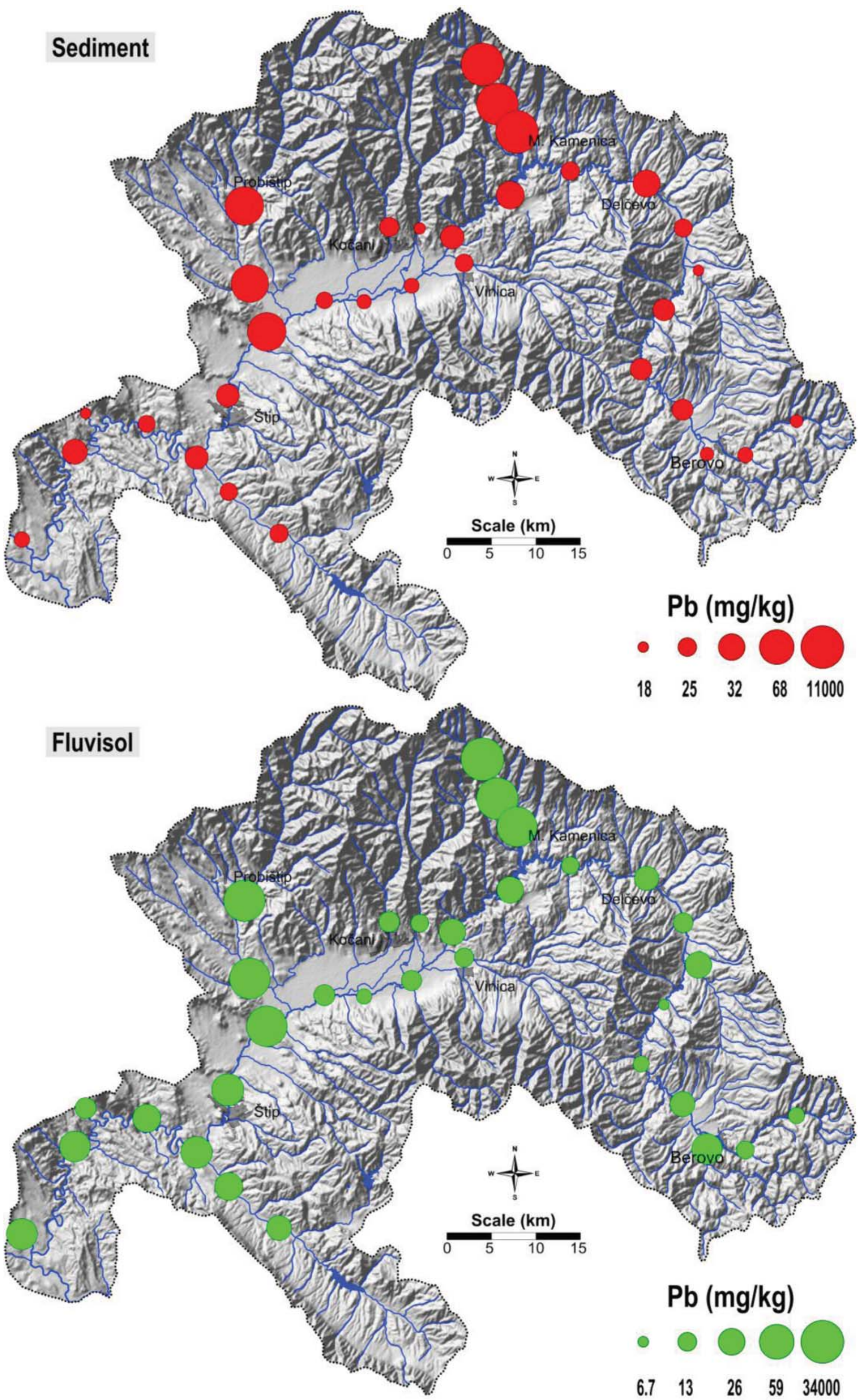

Figure 8. Spatial distribution of lead in the sediment and the fluvisol soil in the Bregalnica river basin.

contents of these elements are also primarily conditioned by the morphological profile of the alluvium. The halogen elements show affinity among each other also in the soil lithogenic structures, on which this association is probably based. There is certain specific trend of enrichment of these elements in Zone 1, where Quaternary alluvium predominates (Fig. 3). This factor is closely correlated with the distribution of the second factor (As-W-Ba-Ag-Cu-Tl-Zn-Sb-Mo-In-Cd-Te-Bi-Pb), i.e. the occurrence of the oldest volcanic rocks has significant influence on both Factors 2 and 3, which clearly points to their inter-correlation, even though they are isolated as separate factors (Fig. 5).

Areal distribution of the geochemical dominant associations

The two dominant geochemical associations are also presented graphically using bar plots, for enhanced visual overview of the distribution. The distribution of the elements of the first

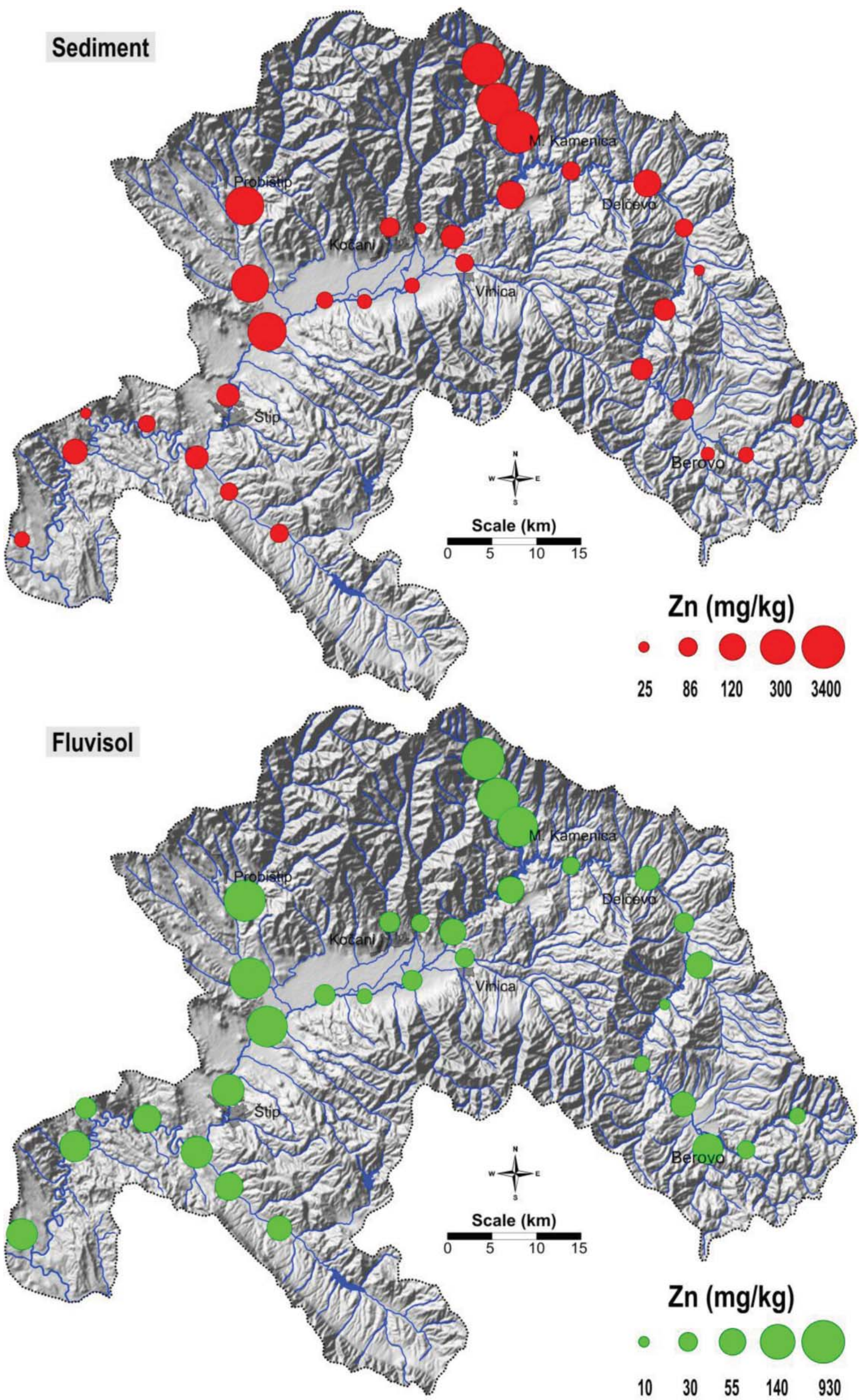

Figure 9. Spatial distribution of zinc in the sediment and the fluvisol soil in the Bregalnica river basin.

geochemical association (F1) in sediments and fluvisol soils is presented in Figure 6. The contents of these elements are almost constant along the whole course of the Bregalnica river both in the sediment and on the river terraces (fluvisol soils). The contents of these elements behave in a similar way in the tributaries, with lower presence in the Kamenička River, Lakavica and the Ovčepolska River (Fig. 6). Usually, sediments are significantly more enriched with lithogenic elements compared to the fluvisol.[2,6,35,36] The geochemistry of large rivers will provide insights to the erosional processes of the study region on a global scale due to the differential mobility taking place between the metals by denudation.[37,38] Water–rock interaction, especially at low temperature is unlikely to cause substantial change in REE distribution in all sediments. Hence the REEs are insoluble with extremely low concentrations in dissolved form in the river and are mainly transported and deposited as detrital materials in the river basins.

The second geochemical association (F2) behaves very similarly to the first as regards the contents of the elements in the sediments and fluvisol soils. Along the whole course of the Bregalnica river a certain continuous trend of the contents of these elements is perceived, with a mild increase in the area after the mouth of the Zletovska River. Unlike Factor 1, the distribution of the second geochemical association in the sediment and the fluvisol soils of the tributaries is significantly more distinguished. Maximum contents of this factor are detected in the sediment of the Kamenička River, and, with a very mild decrease, in the Zletovska River. Cd-Pd-Zn-Sb stand out as dominant variables in this association. High contents of lead and zinc are found both in the sediment and the fluvisol. The pollution of the Kamenička River is alleviated by the presence of the hydro accumulation Kalimanci, which, on its part, acts as an accumulator of the high contents and deposits of the flotation tailings from the mine *Sasa*. The Zletovska River behaves similarly to the Kamenička River, with high contents of the elements of this geochemical association, with particular emphasis on lead and zinc (Fig. 7).

The anthropogenic introduction of Pb and Zn is due to the continuous outpour of wastewaters from the ore and the flotation plants. These deposits are carried by the river water, which introduces them into the river Bregalnica. In this way, the Zletovska River is a more intensively polluted than the Kamenička River, although the maximum contents of lead and zinc are found in the sediment and the alluvium of the Kamenička River. For better visual representation, spatial distribution maps for lead and zinc in the whole investigated areas are provided (Figs. 8 and 9). The sediment represents a natural archive for the geochemistry of the elements. The historical record for the geochemistry of Pb inputs in the river shows significant dominance of Pb in the sediment vs. fluvisol (Fig. 8). This is particularly evident in the content of lead in Zone 3 where the median of this element is significantly reduced in the fluvisol, which is not the case for the sediment. This phenomenon is even more dominant in determining the total Zn content (Fig. 9).

Conclusion

The focus of this paper is on the mapping of the lithogenic and anthropogenic distribution of a total of 69 elements in alluvial soil samples from the Bregalnica river basin. The specific polymetallic enrichments occur in the areas of the very old Neogene volcanism (Makedonska Kamenica, Zone 3) and Oligocene volcanism (Kratovo-Zletovo district, Zone 4). Strong relations occur between these dominant lithological units and the hydrothermal exploitation in the area of the Pb-Zn Sasa mine, the Pb-Zn Zletovo mine and the Bučim copper mine.

Dominant geochemical association of the following elements was presented: Y-Eu-Lu-Cr-V-La-Gd-Nb-Co-Hf-Zr-Ga-Mg-Fe-Sr-Ta-Sn-Li-Na-Rb-Ni-Ge-Be-Cs. This geochemical marker is related to the dominance of Quaternary alluvium along the upper course of the river Bregalnica. The distribution patterns of these metals mainly reflect the lithological control of the drainage basin. This finding is also supported by the abundance of Al, Fe and Mn in the river sediments and the fluvisol. The second dominant geochemical association, As-W-Ba-Ag-Cu-Tl-Zn-Sb-Mo-In-Cd-Te-Bi-Pb, indicates enrichment of certain elements in the areas of mineral Pb-Zn deposits. This may be attributed partly to the weak soil development and lack of soil contamination in the studied zones. On the contrary, Pb and Zn contents are mainly determined by the pedophytogenic controls rather than the lithogenic factors.

The distribution of trace elements within the individual zones showed a relationship to some soil-forming processes (with emphasis on Zn content). Pb contents were strongly correlated with the hydrothermal exploitations especially in the area of very old volcanism (Neogene clastites). The areas of Neogene vulcanites were characterized with the natural enrichments of Fe and Cd, due to the poly-metallic unused area (Berovo-Vladimirovo, poly-metallic anomaly, Zone 1).

This study suggests that the further investigations should be focused on: a) determining the geochemical interaction of the elements between soil horizons, separately in the areas of Neogene volcanism (Sasa mine) vs. Oligocene volcanism (Kratovo-Zletovo); b) quantification of the enrichment factors for the trace elements in topsoil along the Bregalnica river basin, hunting the geochemical markers for this unique geological area.

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