

FISNIK LAHA (ORCID: 0000-0003-3254-6713)<sup>1</sup>

FATBARDH GASHI (ORCID: 0000-0003-4996-7653)<sup>1</sup>

ARBËR MUSLIU<sup>1</sup>

## CHEMICAL ASSESSMENT AND SPATIAL DISTRIBUTION OF SELECTED ELEMENTS IN AQUATIC SEDIMENTS IN THE REGION OF PEJA (KOSOVO)

In Kosovo, the supply of potable water from water sources is represented by about 40%. This study represents the geochemical analyses of sediments, spatial and statistical analyses of major elements in sediments (fraction  $<63 \mu\text{m}$ ) of water sources in the Drini i Bardhë River basin. For a better understanding of the geochemical consistency of sediments, inductively coupled plasma-mass spectrometry (ICP-MS) was used and the amounts of P and S were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). By comparing the concentrations of Ba, Se, and P with the existing criteria, it was found that 26 of 50 sample points exceed recommended norms, which cause low/significant toxic effects and 23 of 50 sample points include anomalies of the analyzed elements. In terms of statistical interpretation, the average concentration of the studied elements decreased in such order:  $\text{Ca} > \text{Al} > \text{Mg} > \text{K} > \text{S} > \text{P} > \text{Na} > \text{Ba} > \text{Sr} > \text{Li} > \text{Rb} > \text{B} > \text{Ga} > \text{Cs} > \text{Be} > \text{Se}$ . In terms of correlation analyses, elements such as Li, Be, Mg, P, and Ba did not show a significant positive correlation with any element. Cluster analysis of *R*-modality shows a branch of dendrogram linked with Ca, Al, Mg, S, K, P, Na, Ba, Sr, Cs, B, Ga, Se, Be, Rb, and Li. Spatial distribution maps of major elements show that high concentrations of Li, Ca, and Ba were located mostly in the northern part, high concentrations of B, Na, Mg, Sr, and Cs were located in the north-east part, high concentrations of Be and Al were located in the north and south part and high concentrations of P, S, K and Rb were located mostly in the south-east part of the catchment basin. This high concentration of elements is impacted by the lithology of rocks and by the minor influence of human activity (the case of P).

### 1. INTRODUCTION

Sediment and water pollution by chemical elements is a crucial environmental and human problem and human activities may induce considerable changes in the physico-

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<sup>1</sup>Department of Chemistry, Faculty of Natural Sciences, University of Prishtina, 10000 Prishtina, Kosovo, corresponding author F. Gashi, e-mail address: fatbardh\_gashi@hotmail.com

chemical properties of aquatic sediments and aquatic sources. Demographic growth and overall economic development increased industrial and agro-productive capacities and producers at the country level by putting increased pressure on the use of groundwater. Groundwater resources represent one of the safest sources of potable water supply. In Kosovo, the supply of potable water from water sources is represented by about 40%. Sediments are integral parts of the aquatic environments because they help to determine the overall assessment of heavy metals in water vis-avis aquatic life and survivability [1]. Bottom sediments in all aquatic environments are reasonable and fact-finding sources of information on processes and mechanisms occurring in aquatic ecosystems. Hydrological cycles, physic-chemical processes, and complex spatiotemporal variations enable the remobilization of heavy metals from sediments into the water. The concentration of heavy metals exceeding norms in the environment can cause environmental and human health problems [2]. Studies on metals in rivers, lakes, fish, and sediments have been a major environmental focus in the last decades. Sediments (silt and clay) containing ecotoxic heavy metals and other inorganic and organic substances are important for studying water pollution, and therefore, their multidisciplinary research is essential for understanding different processes and to understand better the geochemical cycles of different trace elements [3].

The behavior of metals in natural waters is determined by the water chemistry and sediment composition [4]. Heavy metals are regarded as serious pollution of aquatic ecosystems because of their environmental persistence and toxicity effects on living organisms. Some chemical elements are easily transported from the surface to groundwater and the safe water gradually becomes a scarce commodity, due to the mix-up of huge contaminants through natural processes like soil and rock weathering and anthropogenic activities such as industrial effluents, domestic sewage, garbage, over mining activities, explosive population, etc. [5]. Metallic elements are environmentally stable and they can enter the living system through an aquatic medium causing acute adverse effects on human beings, animals, and plants. This work is a continuation of earlier studies of sediments in the area of nearby countries of Kosovo and Croatia [6–9]. The objective of this work is to determine the concentrations of some major chemical elements in sediments (fraction  $<63 \mu\text{m}$ ) of aquatic sources and to create their spatial and temporal distribution maps in the study area.

## 2. STUDY AREA

Geographically Kosovo is located between  $41^{\circ}51' - 43^{\circ}16' \text{ N}$  and  $20^{\circ}01' - 21^{\circ}48' \text{ E}$  and it is mainly situated on two plains; the Dukagjini plain (sea levels 330–550 m) and the Kosovo Plain (sea levels 500–600 m). Drini i Bardhë river basin is the biggest with a surface of  $4.289 \text{ km}^2$  and takes the western part of Kosovo. This area consists of several small streams from the mountains, water flows into tributaries, and the Drini I

Bardhë River. In geotectonic terms, Kosovo is located within the Dinaric mountains and all three divisions of rocks, namely magmatic, sedimentary, and metamorphic of Precambrian to Quaternary Ages are present in the territory of Kosovo. The sediments of the rivers in Kosovo are composed of alluvial deposits containing largely varying proportions from unconsolidated to semi-consolidated sand and gravel materials. In hydrogeological aspects, geological, lithological, structural, and tectonic characteristics, the following areas of aquifers are distinguished in the study area: intergranular porous aquifers, porous cracks, karst porosity, and waterless terrain [10].

### 3. MATERIALS AND METHODS

*Sampling and sample preparation.* In the study area, sediment samples were collected from 50 different locations from November 2018 to January 2019, to assess the concentration of some major elements and to create the spatial distribution of the analyzed elements. The locations of sample points were determined by applying the global positioning system (GPS) device, using a Garmin GPS and locations were well described. The details about the sites are presented in Table 1 and the study area with sampling points sections is shown in Fig. 1.

Table 1

Sampling stations, locality, coordinates, and sea level with detailed locality description

Sample	Locality	Coordinate <i>X</i>	Coordinate <i>Y</i>	Possible pollution sources
P1	Runik	427938	202933	settlement, agriculture land
P2	Banjë e Runikut	424869	204008	settlement, agriculture land
P3	Surigjan	4249112	2038904	settlement, wastewater
P4	Cerkulez	4248422	2038347	settlement, agriculture land
P5	Padalishtë	424731	203853	settlement, agriculture land, wastewater
P6	Rakosh	4247316	203853	settlement, agriculture land, wastewater
P7	Bellopojë	4246136	2034334	settlement, agriculture land, wastewater
P8	Dubravë	4246754	2031355	settlement, agriculture land
P9	Burimi – Istog	4274329	202886	mountain tourism
P10	Burimi – Vrellë	424648	202397	mountain tourism
P11	Radave	4243635	2019644	settlement, agriculture land
P12	Zllakuqan	4239467	2032678	settlement, agriculture land
P13	Ranoc	4240855	2033738	agriculture land, wastewater
P14	Leskoc	4241394	2034992	settlement, agriculture land
P15	Osjan	4243409	2033467	agriculture land, coal source
P16	Berkovë	4240275	2031954	settlement, agriculture land
P17	Zabllaq	4241396	2029643	settlement, agriculture land
P18	Gjurakove	4242285	202905	settlement, agriculture land
P19	Prekallë	4241837	2028288	settlement, agriculture land

Table 1

Sampling stations, locality, coordinates, and sea level with detailed locality description

P20	Trubohovc	4241458	2027578	settlement, agriculture land
P21	Staradran	4241751	2026059	settlement, agriculture land
P22	Kashicë	4242709	2023831	settlement, agriculture land
P23	Fusha e Pejës	4239513	2019206	settlement, agriculture land
P24	Vitomiricë	4241141	2019667	settlement, agriculture land
P25	Dubravë e Vogël	4243167	2022004	settlement, agriculture land
P26	Klinë	423561	2034274	agriculture land, wastewater
P27	Grabanicë	4235725	2032207	settlement, agriculture land
P28	Drenoc	4236379	2031178	settlement, agriculture land
P29	Potërq i ulët	4236373	2030825	agriculture land, wastewater
P30	Potërq i epërm	423679	2030273	agriculture land, wastewater
P31	Jabllanicë e Leshanit	4237089	2028447	agriculture land, wastewater
P32	Kliqinë	4237292	2027433	agriculture land, wastewater
P33	Leshan	4237685	2026971	settlement, agriculture land
P34	Gllaviqicë	4238325	2026483	settlement, agriculture land
P35	Gllaviqicë	4238287	202566	settlement, agriculture land
P36	Vragoc	423774	2024783	agriculture land, wastewater
P37	Millovanc	4237362	2024133	settlement, agriculture land
P38	Gorozhdevc	4238014	2022916	settlement, agriculture land
P39	Potërq	4236918	2029919	settlement, agriculture land
P40	Jabllanicë	4237454	2028234	agriculture land, wastewater
P41	Ramun	4238579	2024992	settlement, agriculture land
P42	Llabjan	4239328	2024266	agriculture land, meat industry
P43	Lutogllavë	4239661	2025829	agriculture land, garbage dump
P44	Ruhot	4240441	2026153	settlement, agriculture land
P45	Terstenik	4240557	202722	settlement, agriculture land
P46	Nabërgjan	424041	2025084	settlement, agriculture land
P47	Nabërgjan i epërm	4240275	2023349	settlement, agriculture land
P48	Nakull	423988	2022435	settlement, agriculture land
P49	Bllagajë	424002	2021492	agriculture land, wastewater
P50	Fusha e Pejës	423995	2020394	settlement, agriculture land

The sediment sampler was washed with water before the next sampling and dried. Sampling was realized at different points; 1–2 kg of sediment was collected to provide enough sediments of a fraction under 63  $\mu\text{m}$ . Fine fraction <63  $\mu\text{m}$  is usually used in environmental studies and is easily transported. Each sampling point has been coded, the sampling material was collected in plastic bags and it was dried in the air for 21 days. Coarse materials were separated using first a 40-mesh sieve, and then a 63  $\mu\text{m}$  sieve Fritsch was used for the separation purpose. The standard sampling method was used for sediment collection [11]. Sediment samples were taken from the bottom of aqua sources (1–5 cm) using the sediment sampler, model Ekman grab with package size of 56×22×40 cm.

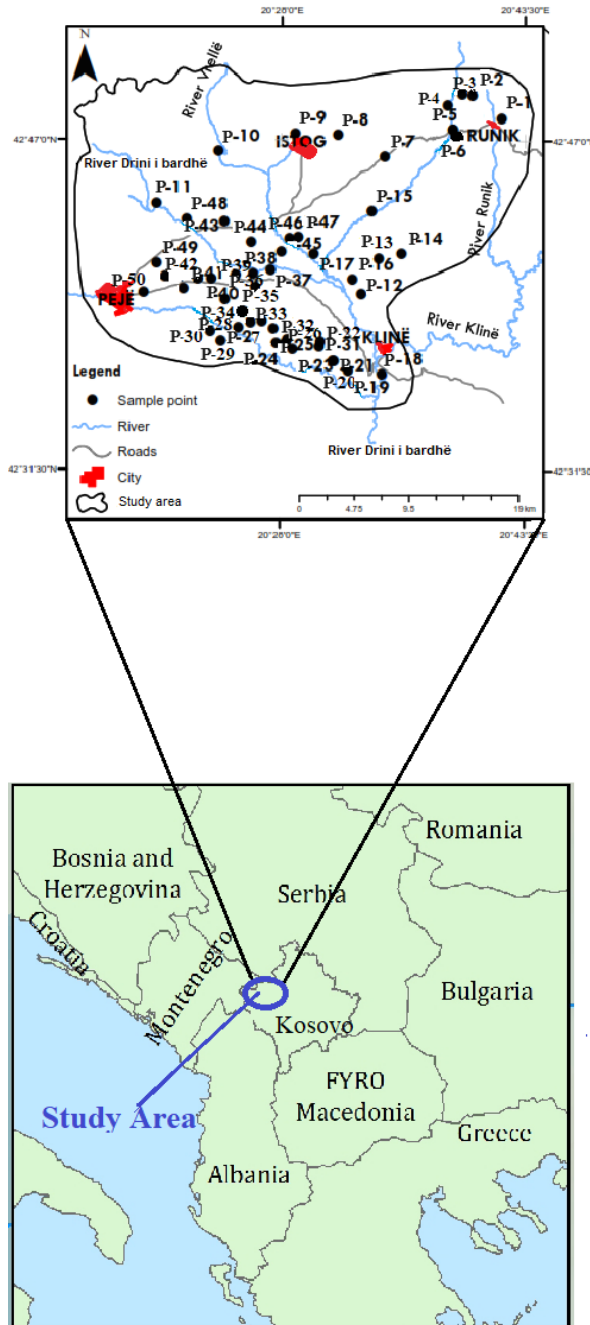


Fig. 1. The investigated area with station points

*ICP-MS and ICP-OES determination of elements.* Inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine the concentration of elements in the sediment samples and the amounts of P and S were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The geochemical analysis of aquatic sediment samples has been done at Actlabs laboratory in Canada, using the Ultra trace 2 testing program. Regarding the testing standard operation procedure, the sample preparation started with 0.5 g of the aquatic sediment sample dissolved in aqua regia at 90 °C in a microwave digestion unit and then the prepared solution was diluted and chemically analyzed with a Perkin Elmer SCIEX ELAN 6100 ICP-MS instrument. For determination, the following reference materials (RM) were used: USGS GXR-1, GXR-2, GXR-4 and GXR-6. Although the digestion of sediment samples is not total, its use is justified because the international standard methods for determining action limits are based on aqua regia leach [12].

*Statistical assessment.* Statistical parameters, 2D box plot diagrams for determination of anomalies for solution data, correlation coefficient, and *Q*- and *R*-mode cluster analyses were performed using Statistical 6 [13]. It was used to assess the sources and distribution of major elements in natural aqua sediments in the study area. Outlier values are between 1.5 and 3 and extreme ones above 3 standard deviations. The principal component analysis (PCA) is considered the main of the multivariate data analysis and it was first formulated by Pearson in statistics, and then was followed by Fisher and MacKenzie [14]. PCA was widely applied to reduce the original variables of the contaminants and to analyze their sources. Correlation analysis was performed to find the mutual dependence of elements. Statistical processing of chemical data and setting up the database, mainly to achieve GIS maps, is an essential phase of sediment quality assessment. *R*-mode, clusters of variables, in our case chemical elements are desired. Cluster analysis of *Q*-modality was applied, to disaggregate it into more homogenous subsets [15], and it was performed to find groups that contain similar/different sediment samples.

*Spatial and temporal distribution of elements in aqua sediments.* The GIS mapping methodology was applied to create spatial distribution maps of major element concentrations. The software “ArcView” version 10.1, was used for spatial distribution mapping of the analyzed major elements in the study area [16].

## 4. RESULTS

### 4.1. CHEMICAL ANALYSES OF ELEMENTS USING ICP-MS METHOD

The result of concentrations of major elements in the aquatic sediment fractions under 63 µm, was determined by using ICP-MS and ICP-OES methods, and are tabulated in Table 2. Sediments from aqua sources were analyzed in a completely randomized design and the limit of detection of used methods for the elements was (in µg/g) Li 0.1 , Be 0.1,

B 1.0, Na 10, Mg 100, Al 100, P 10, S 10, K 100, Ca 100, Rb 0.1, Sr 0.5, Cs 0.02, Ba 0.5, Se 0.1 and Ga 0.02.

Table 2

The concentration of 16 chemical elements in 50 samples of aquatic sediments [ $\mu\text{g/g}$ ]

Element	Li	Be	B	Na	Mg	Al	P	S	K	Ca	Rb	Sr	Cs	Ba	Se	Ga
LD <sup>a</sup>	0.1	0.1	1	10	100	100	10	10	100	100	0.1	0.5	0.02	0.5	0.1	0.02
P 1	15.9	0.9	17	620	23700	21200	510	500	3600	171000	25.9	332	2.84	129	0.9	4.54
P 2	15.4	1	12	260	4600	15200	860	7730	3000	157000	36.3	533	35	222	1.8	3.55
P 3	16.7	0.7	6	220	6100	13200	590	370	2500	212000	15	135	1.86	67	0.2	2.82
P 4	24.4	1	7	290	8600	29200	320	3510	2800	102000	24.3	222	1.88	81.9	0.3	6.64
P 5	24.2	0.8	8	330	7400	20900	240	1830	2100	88600	18.2	112	1.03	90.9	0.3	4.81
P 6	29.9	1.3	4	290	3300	30600	320	40	2600	11700	22.9	84.5	1.61	216	<0.1	7.65
P 7	41.1	1.1	6	290	6900	32500	600	110	3000	5700	19.5	40.8	2.55	107	<0.1	7.23
P 8	44.4	1.5	7	320	7500	37000	460	160	4000	46300	27.5	52.9	3.83	123	<0.1	7.9
P 9	16.3	0.9	6	190	4100	12900	590	220	1900	234000	15.8	92.5	3.63	68.3	0.3	2.83
P 10	36.1	1	10	210	7400	14000	430	220	2300	88900	13.9	74.2	2.15	1090	0.1	<0.02
P 11	32.7	0.9	6	280	6800	24900	660	330	2400	17000	16.4	35.5	2.19	102	0.1	6.15
P 12	17.6	0.9	8	300	5500	20200	970	990	2400	76500	21.2	103	1.32	117	0.2	4.32
P 13	16.6	0.9	6	240	4700	20600	620	1070	2200	68100	16.8	88.8	1.29	90.8	0.3	4.53
P 14	18.2	0.8	11	340	5500	19100	870	730	2400	99000	18.1	117	1.34	137	0.3	4.18
P 15	23.7	1.2	11	250	5200	26000	700	320	4500	30500	31.7	62.6	2.49	164	<0.1	6.21
P 16	29.1	1.2	9	230	6300	20600	1260	400	2600	65600	21.8	136	1.92	292	0.3	3.81
P 17	28.4	1.1	11	230	5800	22600	1660	410	3100	55500	25.4	126	1.95	267	0.3	3.95
P 18	30.2	1.4	7	290	5000	30100	720	270	3800	33700	28.2	80.6	1.99	205	<0.1	6.66
P 19	20.9	1.1	11	350	3600	21400	990	3470	2700	31400	25	59.7	1.62	152	0.7	4.61
P 20	25.3	1.3	7	300	5300	24100	720	1430	3100	37400	25.9	85.2	1.87	163	0.3	5.97
P 21	25.9	1.1	7	260	6400	23700	1120	950	2300	32800	24.4	66	2.18	218	0.2	4.47
P 22	28.6	1.5	15	280	6900	30200	450	720	4500	48000	68.4	135	18.2	318	<0.1	5.48
P 23	29.8	1.6	9	210	5200	22500	320	940	2200	21300	27.8	60.6	4.66	127	0.2	5.14
P 24	25.3	0.9	5	190	5900	13900	350	110	1200	149000	9.8	472	1.24	111	<0.1	3.09
P 25	29	3.4	5	220	8000	16000	260	360	1200	15700	12.2	41.9	1.64	106	<0.1	4.05
P 26	19.8	0.9	5	220	6100	15000	540	370	1700	73800	14.5	185	1.36	98.7	0.2	3.69
P 27	18.1	0.8	6	250	4700	17700	550	4230	1900	101000	17.7	183	1.28	145	0.8	3.81
P 28	24.3	1	6	270	5600	20100	850	750	2000	26800	19.9	57.8	1.93	173	0.2	4.39
P 29	15.9	1	7	340	5100	17800	710	2760	2000	15200	19.3	58.5	1.57	182	0.2	3.75
P 30	17.8	0.9	7	310	5400	23300	770	1280	2000	39800	18.1	139	1.45	206	0.2	3.97
P 31	14	0.3	2	200	12800	8000	420	210	700	106000	4	442	0.57	46.6	<0.1	2.08
P 32	17.7	0.7	3	230	10300	16300	630	300	1600	80400	12.7	281	1.09	91	<0.1	3.35
P 33	17.3	1.2	6	360	11600	13300	430	870	1800	155000	8.2	512	0.91	206	0.1	1.39
P 34	24.4	1.2	2	230	5300	30200	370	150	3500	2900	23.4	17.8	1.44	157	0.2	6.59
P 35	25.1	0.8	5	270	7400	18000	1220	280	2000	37700	15.6	146	1.43	154	0.1	3.93
P 36	22.2	1.9	9	510	12100	19700	550	1720	3000	135000	12.8	311	1.02	370	0.1	1.2
P 37	19.9	0.5	3	230	7800	15400	630	80	1300	6700	7.5	22.1	0.77	50.2	<0.1	3.33
P 38	17	0.7	9	400	7500	15900	480	1200	1400	196000	9.9	250	1.15	152	0.2	3.08
P 39	22.1	1	4	260	5400	23700	640	500	2400	13900	19.5	38.5	1.44	141	<0.1	4.86

Table 2

The concentration of 16 chemical elements in 50 samples of aquatic sediments [ $\mu\text{g/g}$ ]

P 40	16	1	24	770	5500	20200	1400	11220	2400	45200	19.6	97.1	1.52	175	0.6	7.17
P 41	23.5	1	3	210	4300	16900	440	100	1500	7700	13.5	40.9	1.26	75.7	<0.1	4.24
P 42	15.9	0.9	4	190	2400	15500	960	1520	1400	10300	21.6	31.9	1.72	95.5	0.6	4.03
P 43	22	0.6	3	230	6400	13800	600	320	1500	94100	12.7	132	1.11	76.8	<0.1	3.31
P 44	28.9	1.1	8	250	6700	22000	1070	450	4200	21600	25.8	80.8	1.97	136	0.2	5.29
P 45	26.1	0.9	5	250	7700	19400	540	150	2200	62600	15	246	1.85	93.6	<0.1	4.49
P 46	18.6	0.7	20	700	7700	15600	970	1700	2800	101000	14.6	260	1.19	145	0.2	3.31
P 47	25.1	0.9	5	200	7300	17100	530	150	2100	100000	14.3	284	1.55	106	<0.1	4.02
P 48	19.8	0.7	5	220	7400	14200	630	410	1900	91600	14	274	1.19	94.5	0.2	3.36
P 49	25.4	0.9	5	220	7300	17500	540	210	2100	96100	13.6	273	1.46	102	0.2	4.11
P 50	23.1	0.8	8	330	8000	17400	790	850	2200	98600	14.8	211	1.61	157	0.5	3.58

<sup>a</sup>LD is the limit of detection.

## 4.2. STATISTICAL ANALYSES

The results of descriptive statistical analysis for chemical elements in sediment samples are presented in Table 3, and the value of each element is given as arithmetic mean, geometric mean, median, minimal and maximal concentration, variance, and standard deviation based on the total concentration for each element.

Table 3

Basic statistical analyses of 16 elements in the sediment of 50 water sources

Variable	Descriptive statistics						
	Mean	Geometric	Median	Minimum	Maximum	Variance	Std. Dev.
Li	23.3140	22.4866	23.300	14.00	44.4	4.351470E01	6.597
Be	1.0380	0.9732	0.950	0.30	3.4	1.954653E-01	0.442
B	7.5000	6.5498	6.500	2.00	24.0	1.854082E01	4.306
Na	292.8000	276.6395	260.000	190.00	770.0	1.448588E04	120.357
Mg	6870.0000	6392.5793	6350.000	2400.00	23700.0	1.010255E07	3178.451
Al	20132.0000	19314.8120	19 550.000	8000.00	37000.0	3.512549E07	5926.676
P	677.0000	618.2796	610.000	240.00	1660.0	9.098469E04	301.637
S	1179.4000	546.7424	430.000	40.00	11 220.0	3.919924E06	1979.880
K	2400.0000	2252.4198	2250.000	700.00	4500.0	7.289796E05	853.803
Ca	72354.0000	48 383.5327	64 100.000	2900.00	234 000.0	3.269639E09	57 180.760
Sr	158.4640	114.5580	114.500	17.80	533.0	1.706933E04	130.650
Ga	4.3388	3.7375	4.080	0.02	7.9	2.595868E00	1.611
Ba	163.8900	136.9693	136.500	46.60	1090.00	2.240334E04	149.677
Cs	2.7224	1.7838	1.590	0.57	35.00	2.768232E01	5.261
Rb	19.5000	17.7170	18.100	4.00	68.4	9.221878E01	9.603
Se	0.341176	0.262393	0.200000	0.100000	1.800000	0.106738	0.326708



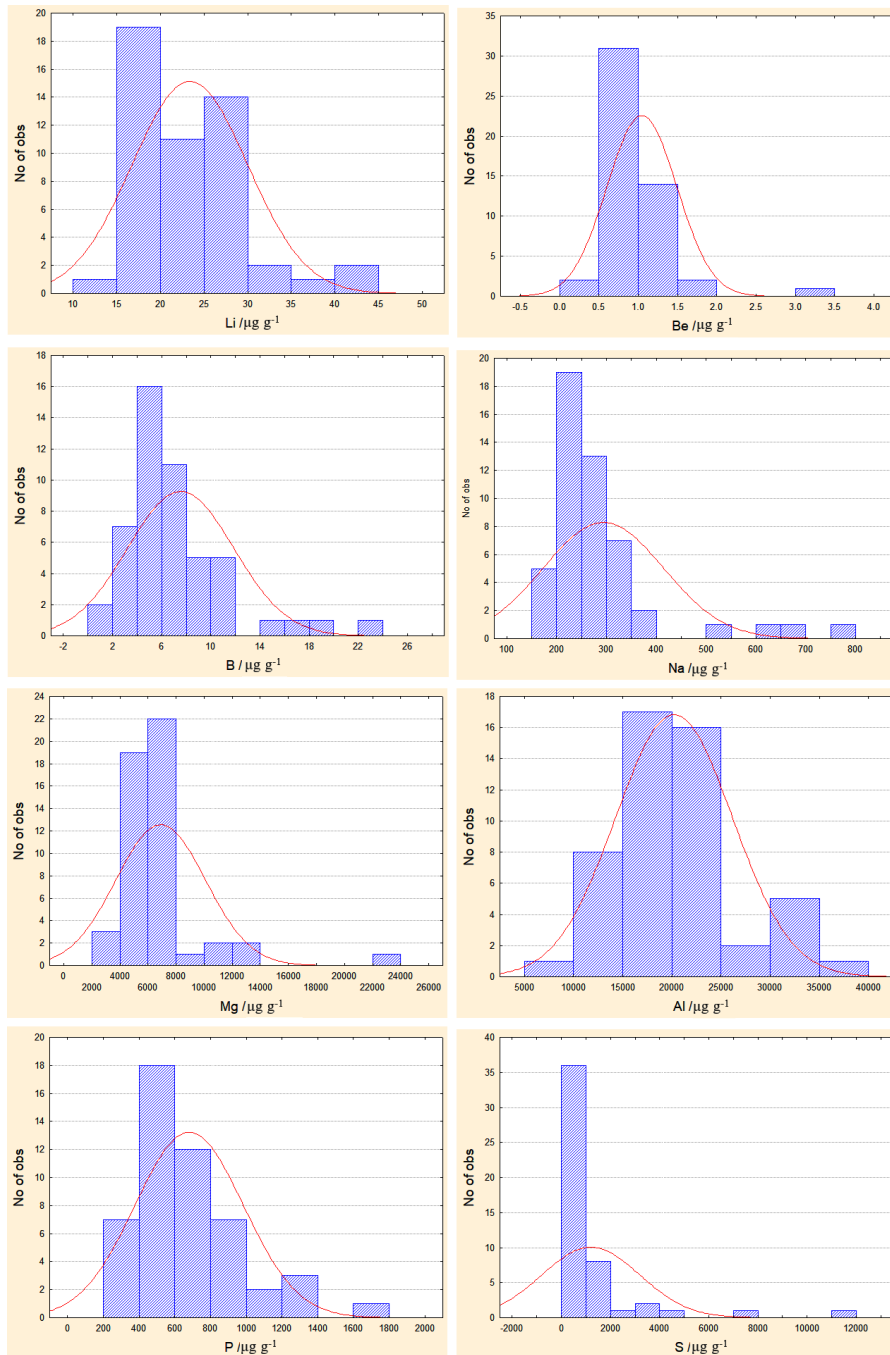


Fig. 2. Frequency histograms of 8 selected elements

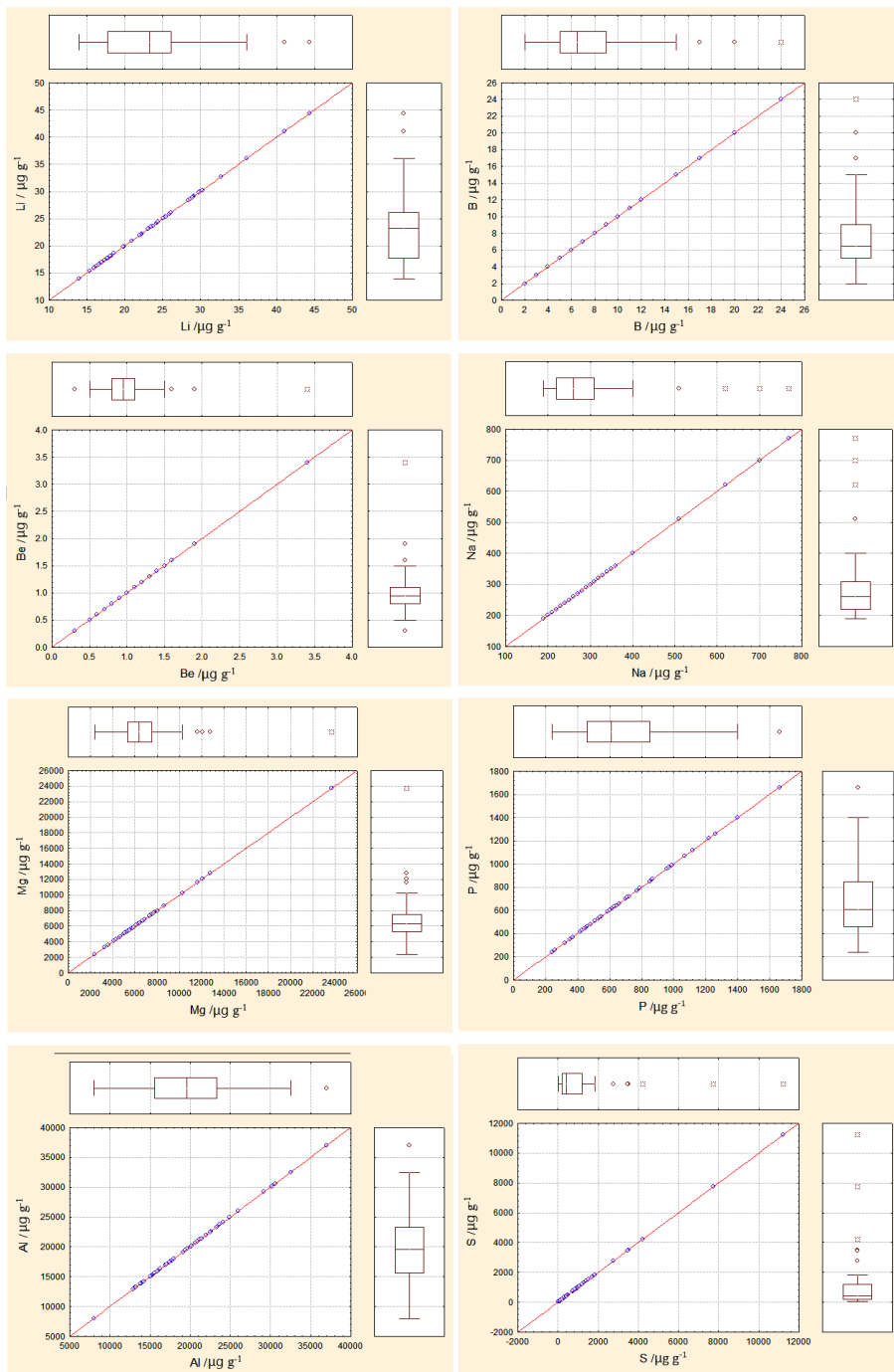


Fig. 3. Scatterplot with plots 2D diagrams of 8 selected elements

Using experimental data from Table 2, frequency histograms and 2D scatter box with plot diagrams [17] for selected elements are presented in Figs. 2 and 3. The anomalous values (outliers and extremes) of elements in all sediment points are presented in Table 4. The relationship between the concentrations (mean values) of these elements was shown by performing correlation analysis and matrix for Pearson's correlation coefficients of selected variables and it is displayed in Table 5. The level of significance was set at  $p < 0.05000$  for all statistical analyses. The clustering techniques *R*- and *Q*-mode have often been applied to a wide variety of research issues [18]. Cluster analyses of *R*-mode cluster the variables, and Fig. 4 shows mutual links between studied elements and observed that an element has the closest association with other elements. Cluster analysis of *Q*-modality was performed on the total set of elements (Table 2) and this analysis shows that sampling points were grouped in 4 clusters. The results of *Q*-modality cluster analysis, with the distances given in parenthesis and means for each cluster, are presented in Tables 6–8.

Table 4  
Sediment points with anomalous values  
of chemical elements

Sample	Extreme values of elements (o)	Outlier values of elements (o)
P 1	Mg, Na	B
P 2	S, Cs	Sr
P 3	–	Ca
P 4	–	S
P 7	–	Li
P 8	Al	Li, Ga, Cs
P 9	–	Ca
P 10	Ba	–
P 15	–	K
P 19	–	S
P 22	Rb, Cs	K, Ba
P 23	Cs	Be
P 25	Be	–
P 27	S	S, P
P 31	–	Mg
P 33	–	Mg
P 36	–	Na, Be, Mg, Ba
P 40	Na, B, S	–
P 44	–	K
P 46	Na	B

Marked correlations are significant at  $p < 0.05$ .

Table 5

Matrix of Pearson's correlation coefficients between elements in aquatic sediments

Symbol	Li	Be	B	Na	Mg	Al	P	S	K	Ca	Rb	Sr	Cs	Ba	Se	Ga
Li	1.00	0.41	-0.10	-0.22	-0.12	0.64	-0.12	-0.35	0.40	-0.44	0.25	-0.38	-0.04	0.31	-0.37	0.44
Be	0.41	1.00	0.06	-0.00	-0.03	0.32	-0.18	-0.03	0.24	-0.27	0.26	-0.23	0.10	0.15	-0.10	0.20
B	-0.10	0.06	1.00	0.79	0.19	0.11	0.41	0.58	0.45	0.16	0.41	0.08	0.27	0.25	0.39	0.12
Na	-0.22	-0.00	0.79	1.00	0.39	0.09	0.25	0.52	0.24	0.15	0.03	0.14	-0.05	0.04	0.22	0.12
Mg	-0.12	-0.03	0.19	0.39	1.00	-0.14	-0.22	-0.15	0.05	0.37	-0.15	0.49	-0.10	0.02	0.03	-0.25
Al	0.64	0.32	0.11	0.09	-0.14	1.00	-0.01	-0.05	0.72	-0.51	0.60	-0.47	0.06	0.01	-0.13	0.84
P	-0.12	-0.18	0.41	0.25	-0.22	-0.01	1.00	0.32	0.17	-0.18	0.13	-0.16	0.03	0.05	0.24	0.04
S	-0.35	-0.03	0.58	0.52	-0.15	-0.05	0.32	1.00	0.04	0.07	0.17	0.15	0.40	0.02	0.67	0.14
K	0.40	0.24	0.45	0.24	0.05	0.72	0.17	0.04	1.00	-0.17	0.75	-0.21	0.31	0.20	0.11	0.53
Ca	-0.44	-0.27	0.16	0.15	0.37	-0.51	-0.18	0.07	-0.17	1.00	-0.23	0.66	0.16	0.00	0.27	-0.54
Rb	0.25	0.26	0.41	0.03	-0.15	0.60	0.13	0.17	0.75	-0.23	1.00	-0.21	0.61	0.15	0.26	0.48
Sr	-0.38	-0.23	0.08	0.14	0.49	-0.47	-0.16	0.15	-0.21	0.66	-0.21	1.00	0.31	-0.05	0.31	-0.47
Cs	-0.04	0.10	0.27	-0.05	-0.10	0.06	0.03	0.40	0.31	0.16	0.61	0.31	1.00	0.13	0.65	0.03
Ba	0.31	0.15	0.25	0.04	0.02	0.01	0.05	0.02	0.20	0.00	0.15	-0.05	0.13	1.00	-0.02	-0.35
Se	-0.37	-0.10	0.39	0.22	0.03	-0.13	0.24	0.67	0.11	0.27	0.26	0.31	0.65	-0.02	1.00	-0.01
Ga	0.44	0.20	0.12	0.12	-0.25	0.84	0.04	0.14	0.53	-0.54	0.48	-0.47	0.03	-0.35	-0.01	1.00

$N = 50$  (case wise deletion of missing data).

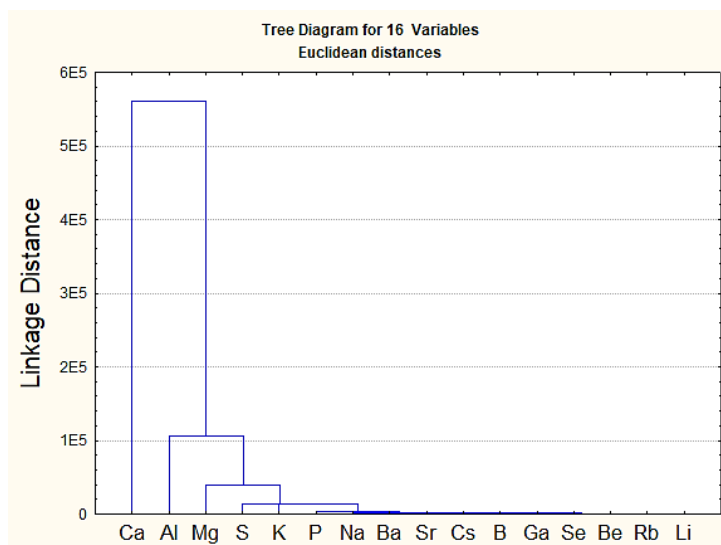


Fig. 4. Cluster analysis *R*-mode. Dendrogram of studied 16 elements

Table 6

Members of 4 clusters (*Q*-mode) and distances of samples from a respective cluster center

Cluster	Members of clusters; distances in parentheses		
Cluster 1 9 cases	P8 (4987.885)	P12 (4143.869)	P13 (2107.552)
	P16 (1510.226)	P17 (1239.316)	P22 (3594.026)
	P26 (3957.649)	P40 (4491.849)	P45 (1199.546)
Cluster 2 14 cases	P4 (3177.052)	P5 (2711.038)	P10 (2611.084)
	P14 (818.7068)	P27 (1277.807)	P31 (3186.200)
	P32 (4630.059)	P36 (9147.866)	P43 (1516.313)
	P46 (743.1777)	P47 (451.0308)	P48 (1950.523)
	P49 (732.1495)	P50 (120.5278)	
Cluster 3 7 cases	P1 (4844.965)	P2 (6537.042)	P3 (7558.003)
	P9 (13 075.48)	P24 (8305.399)	P33 (6797.455)
	P38 (3534.898)		
Cluster 4 20 cases	P6 (3102.357)	P7 (4553.085)	P11 (1183.175)
	P15 (2567.122)	P18 (3691.737)	P19 (2752.325)
	P20 (4122.832)	P21 2972.406)	P23 (183.5928)
	P25 (2255.879)	P28 (1600.421)	P29 (1971.221)
	P30 (4708.081)	P34 (4902.629)	P35 (4372.159)
	P37 (4070.020)	P39 (1791.155)	P41 (3655.738)
	P42 (3339.006)	P44 (578.6340)	

The distance of a cluster member (sample) from the center of the respective cluster group is given in parentheses (refers to Table 7 as well).

Table 7

Euclidean distances between clusters

Cluster number	No. 1	No. 2	No. 3	No. 4
No. 1	0.00	95 208780	931 864 800	96 068 970
No. 2	9757.50	0	433 657 700	380 119 500
No. 3	30 526.46	20 824	0	1 624 743 000
No. 4	9801.48	19 497	40 308	0

Distances below diagonal, squared distances above diagonal.

Table 8

Means of major elements in the clusters

Variable [ $\mu\text{g}\cdot\text{g}^{-1}$ ]	Cluster No. 1	Cluster No. 2	Cluster No. 3	Cluster No. 4
Li	25.18	22.06	17.7	25.32
Be	1.10	0.85	0.9	1.19
B	10.00	7.29	8.7	6.10
Na	315.56	304.29	320.0	265.00

Table 8

Means of major elements in the clusters

Mg	6222.22	8064.29	9071.4	5555.00
Al	22 866.67	17 178.57	15 085.7	22 735.00
P	877.78	576.43	544.3	703.50
S	1721.11	1170.71	1571.4	804.50
K	2788.89	2100.00	2200.0	2505.00
Ca	60 177.78	98 735.71	182 000.0	20 990.00
Rb	25.58	14.69	17.3	20.91
Sr	129.98	226.87	332.4	62.53
Cs	3.69	1.32	6.7	1.89
Ba	175.01	195.26	136.5	146.52
Se	0.24	0.24	0.5	0.20
Ga	5.04	3.41	3.0	5.13

#### 4.3. SPATIAL AND TEMPORAL DISTRIBUTION OF ELEMENTS IN AQUA SEDIMENTS

The spatial and temporal distribution of elements observed in all sediment samples are presented in Figs. 5 and 6.

## 5. DISCUSSION

### 5.1. DISCUSSION OF ICP-MS AND ICP-OES ANALYSES

Geochemical data from Table 2 can be used for the assessment of sediment quality and contamination by chemical elements. Results of chemical analyses were used to compare the obtained amounts of elements with the existing criteria for sediment quality by Société Minière du Sud Pacifique (SMSP) [19] referred further.

Excessive concentration of phosphorus is the most common cause of eutrophication in freshwater lakes, reservoirs, streams, and the headwaters of estuarine systems. The amount of P present in sediment depends on both the external phosphorus load and its release and retention in the sediments. Sediments act as a sink where P can be stored, and also as a source of P for the overlying water. Anthropogenic sources of phosphorus include sewage and industrial effluent, although diffused phosphorus is predominantly of agricultural origin [20]. Concentrations of phosphorus in all samples were lower than the recommended norms from 2000 µg/g in aqua sediments that cause significant toxic effects. Our analyses showed that P in 25 sample points (P2, P7, P11–21, P28–P30, P32, P35, P37, P39, P42, P44, P46, P48 and P50) exceeds the recommended norms from 600 µg/g that cause low toxic effects and make the aquatic life unsuitable. The high concentration of P is probably due to natural (present in the earth's crust) and anthropogenic factors (excessive use of chemical fertilizers in agricultural lands in this area).

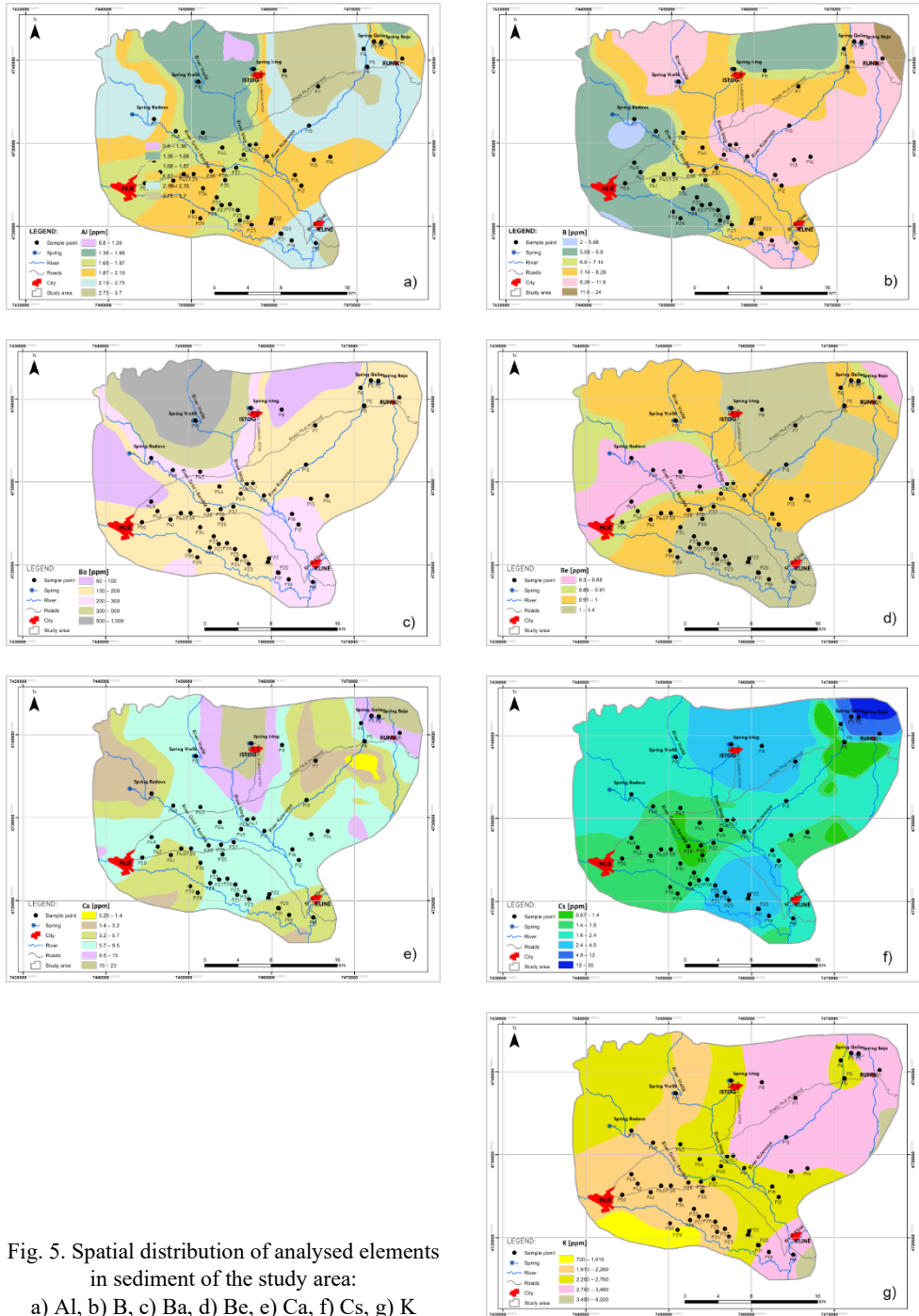


Fig. 5. Spatial distribution of analysed elements in sediment of the study area:  
 a) Al, b) B, c) Ba, d) Be, e) Ca, f) Cs, g) K

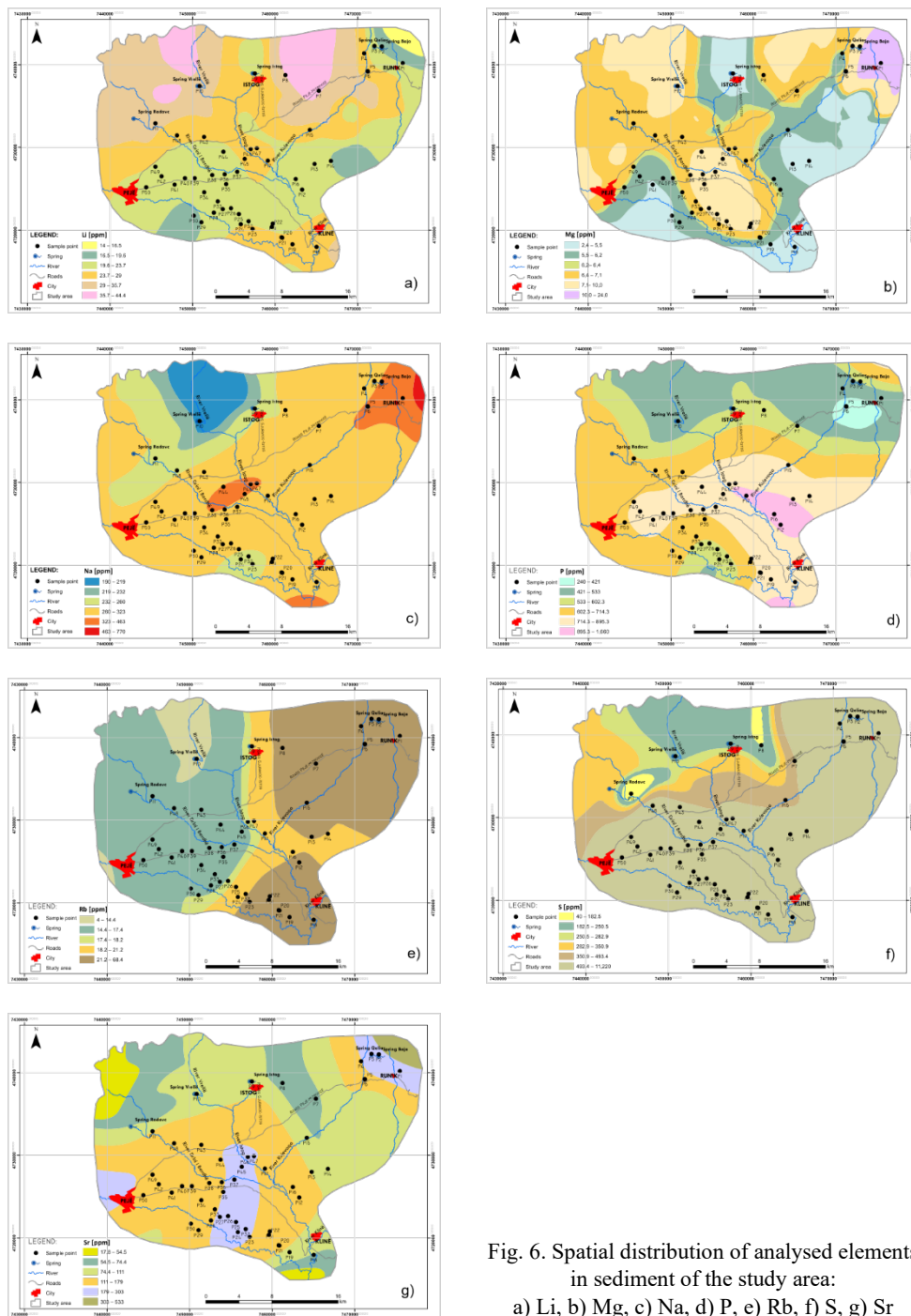


Fig. 6. Spatial distribution of analysed elements in sediment of the study area: a) Li, b) Mg, c) Na, d) P, e) Rb, f) S, g) Sr



*Selenium (Se)* is present in earth's crust, often in association with sulfur-containing minerals. Selenium is an essential trace element, and food such as cereals, meat, and fish are the principal source of selenium in the general population. Levels Se in food also vary depending on geographical area of production. Selenium is a component of metal sulfide ores, where it partially replaces the sulfur. Bottom sediments are the dominant sink for selenium in aquatic ecosystems via association with suspended particulate matter and subsequent deposition [21]. In our study, Se with concentrations from 1.8  $\mu\text{g/g}$  (in the sample point P2), was found to be higher than recommended norms in aqua sediments from 1  $\mu\text{g/g}$  (causing significant toxic effects), probably from the chemical composition of the earth's crust in that area.

*Barium (Ba)* is a trace element in both igneous and sedimentary rocks. Its compounds are used in a variety of industrial applications; however, barium in water comes primarily from natural sources. Ba is surprisingly abundant in earth's crust (as barite ore), high amounts of Ba may only be found in soils and food (nuts, seaweed, fish, and certain plants). The extensive use of barium in the industry and human activities increases the release of barium in the environment. Our comparative analysis shows that barium in two station points (P31 and P37) exceeds the recommended norms of 60  $\mu\text{g/g}$  causing significant toxic effects. However, only in the sample station P10 (1090  $\mu\text{g/g}$ ), the content of Ba exceeds the recommended norms of 500  $\mu\text{g/g}$ , which means the removal of sediment from the water sources.

The average concentrations of Na, Mg, and Ca in the present study were lower than the average value that was presented by Frančišković-Bilinski [22] for sediments of the Kupa River drainage basin, in Croatia.

*Sodium (Na)* is correlated with terrigenous origin. Sodium exists in some forms of minerals such as feldspars, sodalite, and rock salt. Most salts of Na are highly water-soluble. Sodium content ranged from 190 to 770  $\mu\text{g/g}$ , with an average value of 293  $\mu\text{g/g}$  and the highest value at sample point P40.

*Magnesium (Mg)* and *calcium (Ca)* occur in nature in various minerals such as dolomites and high Mg-calcite. They may be present in amphiboles pyroxenes and such as limestone (calcium carbonate), gypsum (calcium sulfate), and fluorite (calcium fluoride). Magnesium content ranged from 2400 to 23700  $\mu\text{g/g}$  with the arithmetic mean value 6870  $\mu\text{g/g}$  and the highest value at sample point P1 as a sign of rock Ni-mineral most as magnesium-iron silicates [23]. The statistical analysis shows a sample point P1 with extreme values of Mg and outlier values at sample points P31, P33, and P36 as a sign of rock composition in that area. Calcium content ranged from 2900 to 23 4000  $\mu\text{g/g}$  with an average value 72 360  $\mu\text{g/g}$ , standard deviation 57 200  $\mu\text{g/g}$ , and the highest value at sample point P9 as a sign of rock composition in that area. The statistical analysis shows a sample point P9 with outlier values of Ca and this is probably influenced by the consistency of the earth's lithology.

The average concentrations of Al, S, K, Rb, Sr, Li, Cs, Ga, and Be in the present study were higher than the average value that was presented by Frančišković-Bilinski [22] in the study of sediments of the Kupa River drainage basin, Croatia.

*Aluminum (Al)* is released into the environment mainly by natural processes, mainly from soil–water interactions, and the composition of the underlying geological materials [24]. The content of aluminum ranged from 8000 to 37 000  $\mu\text{g/g}$  with the arithmetic mean value 20132  $\mu\text{g/g}$  and the highest value was reached at station point P8. The statistical data in Figs. 2 and 3 shows a sample point P8 with outlier values of Al and this is probably influenced by the consistency of the earth's lithology.

*Sulphur (S)* ranged from 40 to 11220  $\mu\text{g/g}$  with an average value 1180  $\mu\text{g/g}$  and the highest value 11 220  $\mu\text{g/g}$  at sample point P40. The statistical data in Table 2 and frequency histograms and 2D scatter box plot diagrams presented in Figs. 2 and 3 show sample point P2, P27, and P40 with extreme values of sulfur and outlier values at sample points P4, P18, and P19. This may be influenced by the consistency of the earth's lithology.

*Potassium (K)* is correlated with the terrigenous origin and in our study it ranged from 700 to 4500  $\mu\text{g/g}$ , with an average value 2400  $\mu\text{g/g}$ , and the highest value at sample point P22. The analyses of frequency histograms (Fig. 2) and 2D scatter box plot diagram (Fig. 3) show outlier values at sample points P15, P22, and P44 influenced by the consistency of the earth's crust. The concentration of K according to the present study was lower than the value presented by Mona et. al. of sediments of Edku and Mariut Lakes, North Egypt [25].

*Rubidium (Rb)* is correlated with terrigenous origin and in our study it was 4–68.4  $\mu\text{g/g}$  with an average value of 19.5  $\mu\text{g/g}$  and the highest value at P22. The analyses of 2D scatter box plot diagram show an extreme value at P22 probably from the chemical composition of the earth's crust. *Strontium (Sr)* ranged from 17.8 to 533  $\mu\text{g/g}$  with an average value of 158.46  $\mu\text{g/g}$ . *Lithium (Li)* is a tracer of weathering at the Earth's surface, ranging from 14 to 44.4  $\mu\text{g/g}$  with an average value of 23.314  $\mu\text{g/g}$ . 2D scatter box plot diagram of Li shows two outlier values at sample points P7 and P8 as signs of natural geochemical pollution. Using comparative analysis, *Cesium (Cs)* ranged from 0.57 to 35  $\mu\text{g/g}$  with an average value of 2.72  $\mu\text{g/g}$ , standard deviation of 5.26  $\mu\text{g/g}$  and highest value at sample point P2. Using experimental data from Table 2, and frequency histograms and 2D scatter box plot diagrams, we found two sample points (P2 and P22) with extreme values of Cs and an outlier value at P8.

*Gallium (Ga)* does not occur as a free element in nature but as Ga(III) compounds in trace amounts in zinc ores and bauxite. In our study, gallium ranged from less than 0.02 to 7.9  $\mu\text{g/g}$  with an average value of 4.34  $\mu\text{g/g}$  and the highest value at sample point P8. Scatter box plot diagrams (Fig. 3) show an outlier value at the sample point in P6. *Beryllium (Be)* does not occur as a free element in nature but in concentrated silicate minerals relative to sulfides and feldspar minerals relative to ferro-magnesium minerals. In water, at pH 7.5 only a small amount of beryllium may be found in a soluble form [26]. In

our study, Be ranged from 0.3 to 3.4  $\mu\text{g/g}$  with an average of 1.038  $\mu\text{g/g}$ . 2D scatter box plot diagram of Be shows an extreme value at P25 and two outlier values at sample points P23 and P36 probably from the chemical composition of the earth's crust.

*Boron (B)* is concentrated on Earth by the water-solubility of its more common naturally occurring compounds, the borate minerals. In natural waters, boron exists primarily as undissociated boric acid with some borate ions. High-concentration boron ions may be adsorbed by soils and sediments; their adsorption depends on pH [27]. B contents ranged from 2 to 24  $\mu\text{g/g}$  with an average of 7.5  $\mu\text{g/g}$ . 2D scatter box plot diagram of B shows an extreme value at P40 and two outlier values at sample points P1 and P46 probably from the chemical composition of the earth's crust and as a result of wastewater discharges, because borate compounds are ingredients of domestic washing agents.

The average value of 16 examined elements, in the sediments of aqua sources, in this study area follow this trend:  $\text{Ca} > \text{Al} > \text{Mg} > \text{K} > \text{S} > \text{P} > \text{Na} > \text{Ba} > \text{Sr} > \text{Li} > \text{Rb} > \text{B} > \text{Ga} > \text{Cs} > \text{Be} > \text{Se}$ .

## 5.2. STATISTICAL INTERPRETATION OF THE RESULTS

The descriptive statistics of 16 elements in the sediment, a fraction under 63  $\mu\text{m}$ , are presented in Table 3 and the statistical values are given as arithmetic mean, geometric mean, median, minimal and maximal concentration, variance, and standard deviation. Using experimental data from Table 2 and the box plot approach of Tukey, anomalous values (extreme and outlier) of all analyzed elements were determined. Analyzing the frequency histograms and scatter box plot diagrams (Figs. 2 and 3), extreme and outlier values of measured elements were defined and they are presented in Table 4. 23 sample points include anomalies (outlier and extreme) values for the analyzed elements. Correlation Pearson's analysis of elements was calculated to see if some of the parameters were interrelated with each other. In terms of correlation analyses (Table 5) elements such as; Li, Be, Mg, P, and Ba did not show a significant positive correlation with any element. But, B was significantly positively correlated with Na (0.79), whereas Al was with K (0.72) and Ga (0.84). S showed a significant positive correlation with Se (0.67), whereas K was with Al (0.72) and Rb (0.75). Ca showed a significant positive correlation with Sr (0.66) whereas Cs was with Se (0.65).

Cluster analysis (CA) is another type of classification that clusters chemical elements (*R*-mode) and sample points (*Q*-mode) in terms of their similarities or differences. Cluster analysis (*R*-mode) shows a dendrogram (Fig. 6) where all sixteen chemical elements were grouped into one statistically significant cluster. Dendrogram shows mutual links between studied variables, and it could be observed that Ca has the closest association with Al. After that, Al has the closest association with Mg and they form one branch of the dendrogram linked with the other one, in which S, K, P, Na, Ba, Sr, Cs, B, Ga, Se, Be, Rb, and Li follows. These correlations are highlighted, suggesting similar sources

and similar geochemical processes that could control the occurrence of these elements in analyzed sediments (a fraction under 63  $\mu\text{m}$ ).

CA of *Q*-modality was performed on the total set of geochemical data from Table 2 and samples were grouped in 4 clusters (Table 6). The results of the *Q*-modality cluster analysis, with the Euclidian distance and means value of elements in each cluster are given in parentheses (Tables 7 and 8). In the case of 4 clusters, cluster 1 contains 9 sample points, cluster 2 contains 14 sample points, the smallest cluster 3 contains 7 sample points, and the biggest one – cluster 4 contains 20 sample points.

### 5.3. SPATIAL DISTRIBUTION OF CHEMICAL ELEMENTS IN AQUATIC SEDIMENTS

Determination of major elements and their spatial variations is crucial for a better understanding of pollution sources. Spatial distribution maps of major chemical elements (Li, Be, B, Na, Mg, Al, P, S, K, Ca, Rb, Sr, Cs, and Ba) are presented in Figs. 5 and 6 and they show high concentrations of analyzed elements in different parts of the study area. By analyzing the created maps, the high concentrations of Li, Ca, and Ba were located mostly in the northern part, whereas the high concentrations of B, Na, Mg, Sr, and Cs were located mostly in the northeast part of the catchment basin. Also, the spatial maps, show that high concentrations of Be and Al were located mostly in the northern and southern parts, whereas high concentrations of P, S, K, and Rb were located mostly in the southeastern part of the catchment basin.

## 6. CONCLUSIONS

This study represents the geochemical, spatial, and statistical analyses of major elements in sediments (fraction <63  $\mu\text{m}$ ) of water sources in the Drini I Bardhë River basin. In terms of statistical interpretation, the arithmetic mean concentrations of the studied elements decreased in such order:  $\text{Ca} > \text{Al} > \text{Mg} > \text{K} > \text{S} > \text{P} > \text{Na} > \text{Ba} > \text{Sr} > \text{Li} > \text{Rb} > \text{B} > \text{Ga} > \text{Cs} > \text{Be} > \text{Se}$ . According to the existing criteria for sediment quality, Ba, Se, and P in some sample stations exceed recommended norms that cause low or significant toxic effects, making aquatic life unsuitable. Using the frequency histograms and scatter box plot diagrams, it was found that 23 sample points include anomalies (outlier and extreme) of measured elements.

In terms of correlation analyses, elements such as Li, Be, Mg, P, and Ba did not show significant positive correlations with any element. But B was significantly positively correlated with Na, whereas Al was with K and Ga. S showed a significant positive correlation with Se whereas K was with Al and Rb. Ca showed a significant positive correlation with Sr, whereas Cs was with Se. Cluster analysis of *R*-modality shows a Tree diagram where all elements were grouped into one statistically significant cluster and we observed that Ca has the closest association with Al. After that, Al has the closest association

with Mg and they form one branch of the dendrogram linked with; S, K, P, Na, Ba, Sr, Cs, B, Ga, Se, Be, Rb, and Li. Results of cluster analysis *Q*-mode (in case of 4 clusters) show that cluster 1 contains 9 sample points, cluster 2 contains 14 sample points, the smallest cluster 3 contains 7 sample points, and the biggest cluster 4 contains 20 sample points.

Spatial distribution maps of major elements show high concentrations of analyzed elements in different parts of the study area. The high concentrations of Li, Ca, and Ba were located mostly in the northern part, the high concentrations of B, Na, Mg, Sr, and Cs were located mostly in the northeastern part, the high concentrations of Be, and Al were located mostly in the northern and southern part and high concentrations of P, S, K, and Rb were located mostly in the southeastern part of the catchment basin. By comparing the concentrations of Ba, Se, and P with the existing criteria, it was found that at sample points P2, P7, P11–21, P28–32, P35, P37, P39, P42, P44, P46, P48, and P50 they exceed recommended norms that cause low/significant toxic effects. Using scatter box plot diagrams, 23 sample points (P1, P2, P4, P6–10, P15, P17–19, P22, P23, P25, P27, P31, P33, P36, P40, P44, P46, and P50) were found to include anomalies of analyzed elements, probably impacted by the lithology of rocks and from minor influence of human activity (the case of P from the overuse of chemical fertilizers in agricultural lands in this area). The authors of this paper suggest that this study will be useful for the authorities who have responsibility for the natural resources.

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