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Evaluation of sediments quality and geospatial distribution of heavy metals in aquatic sources in the Drini i Bardhë river basin

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Abstract

The purpose of this research study is to determine the concentrations of heavy metals in sediments (fraction <63 µm) from the aquatic sources in the Drini i Bardhë river basin and such research work to be reflected through geospatial distribution maps of heavy metals in the study area. For better understanding of the geochemical consistence of aqua sediments, ICP-MS and CV-AAS techniques were used. Evaluation of the sediment quality was performed by using comparative sediment quality guidelines. The sampling sites were geographically positioned and geospatial distribution maps were created as contribution of the heavy metal pollution in sediments. The results has shown significant differences in the concentration of heavy metals at various sediment sample points. By comparing such concentrations of heavy metals in sediment with the existing criteria, it was found that sample points P1, P2, P4-P12, P16, P17, P22, P23, P25, P26, P30, P35, P40, P42 and P46 were significantly polluted and exceeded mass concentrations at certain studying sample points. In terms of statistical interpretations, the flow concentration of the studying elements has gone according to this ranking Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > As > Sn > Mo > Sb > Cd > Bi > Ag > Hg. Based on the findings from this study, studied area is directly impacted from the geological constitution of rocks (clastic, alluvium, proluvium, glacigene, calc tufa/travertine and lake sediments) and there is a minor influence by the human activity (in the case of iron concentration level).

Keywords: *Heavy metals, Sediment quality, Geospatial distribution, ICP-MS and CV-AAS, Drini Bardhë river basin, Aquatic sources.*

1. Introduction

Sediment and water pollution by metals is one of most environmental-human problems and human activities may induce considerable changes in the physical-chemical properties of aquatic sediments and aqua sources in the Drini i Bardhë river basin. 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]. The concetration of heavy metals in exceeding norms in the environment can cause environmental and human health problems [2-4]. Studies on metals in rivers, lakes, fish and sediments have been a major environmental focus especially in the last decades [5]. Bottom sediments in all aquatic environments are reasonable and fact-finding sources of and information on processes and mechanisms occurring in aquatic ecosystems [6]. Hydrological cycles, physical-chemical processes, and complex spatiotemporal variation enable remobilization of heavy metals from sediments into the water [7]. 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 [8]. The behavior of the metals in natural waters is determined by the water chemistry and sediment composition [9]. Heavy metals are regarded as serious pollution of aquatic ecosystem because of their environmental persistence and toxicity effects on living organisms [10]. In the aquatic environment, the trace elements are partitioned among various environmental components (water, suspended solids, sediments and biota) [11]. Heavy metals are significant environmental pollutants, and their ecotoxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons [12]. Heavy metals have the largest availability in soil and aquatic ecosystems and to a relatively smaller proportion in atmosphere as particulate or vapors. Heavy metals are very stable, they can accumulate in the food chain causing adverse effects on human health and the aquatic ecosystem disturbing the food chain [13]. Heavy metals are discharged into a natural system by natural or anthropogenic sources during their transport and are distributed between the aqueous phase and bed sediments and as result of adsorption, hydrolysis, and co-precipitation only a small concentration of free metal ions stay dissolved in water and the most quantity of them gets deposited in the sediment [14, 15]. Geochemical study of trace elements like Cu, Pb, Co, Cr, Ni, Zn, and Cd could provide a hydrogeochemical framework for assessing the sources and mechanism of metal input, enrichment, and distribution in sediments [16]. Some heavy metals such as Cu, Fe, Mn, Ni and Zn are compulsory as micro nutrients for flora/fauna and microbes. Some of the heavy metals are easily transported from surface to ground water [17] and the drink and safe water gradually becomes scarce commodity, due to mixing up of huge contaminants through natural processes like soil and rock weathering and anthropogenic activities such as industrial effluents, domestic sewage, garbage, over mining activity, explosive population etc. [18]. Metallic elements are environmentally stable and they can enter the living system through an aquatic medium, resulting acute adverse effects on human being, animals and plants. Gashi et al. [19] performed a study of mineralogical/geochemical composition and the investigation of contamination status of stream sediments from main rivers (Drini i Bardhë, Morava e Binçës, Lepenc, and Sitnica). Gashi et al. [20, 21] investigated the distribution of some heavy metals (Cu, Pb, Cd, Zn and Mn) in waters of the main rivers of Kosovo and identified heavily contaminated locations of sediments. Two years later, Gashi et al. [22] investigated the distribution of heavy metals in sediments from the Drenica river and based on the content of heavy metals sediments from the Drenica River has been influenced of various factors with te main impact from urban flows, pollutants from wastewater discharges, as well as infiltration from agriculture and emissions from a nickel refining site. The aim of the current work is to extend our first research on geochemical and contamination status of the sediment fraction, <63 µm, in Drini i Bardhë watershed. At the same time, the geospatial distribution maps of heavy metals in sediment of aqua sources will be created. Advanced statistical methods will be

used to identify hot spots, where intensive monitoring and possibly remediation will be suggested with an objective to create a sustainable human environment.

2. Study area

2.1. *Description of the study area*

Geographically Kosovo is located between 41°51'-43°16' N and 20°01'-21°48' E, and it is mainly situated on two plains; the Dukagjini plain (sea levels 330-550m) and the Kosovo Plain (sea levels 500-600m). The Drini i Bardhë river basin is the biggest with surface of 4.289 km^2 and takes the westem part of Kosovo. The area consist from the seeveral small mountaints streams, water flows into tributaries and Drini i Bardhë river. In geotectonic terms, Kosovo is located within the Dinaric Mountains and all three divisions of rocks, namely magmatic, sedimentary and methamorphic of Precambrian to Quaternary ages are present in the territory of Kosovo [23].

The sediments of the rivers in Kosovo are composed of alluvial deposits containing largely varying proportions of unconsolidated to semi consolidated sand and gravel materials [24]. In the hydro-geological aspects, geological, lithological, structural and tectonic characteristics, the following areas of the aquifers are distinguished in the study area: intergranular porous aquifers, porous cracks, karst porosity and waterless terrain [25]. The area consist from the seeveral small mountaints streams, water flows into tributaries and Drini i Bardhë river.

3. Materials and methods

3.1. *Sampling and sample preparation*

In the study area, sediment samples were collected from 50 different locations during November 2018 - January 2019, in order to assess the concentaration of heavy metals and to create the geospatial distribution of the analysed heavy metals. The standard sampling method was used for sediment collection [26]. Sediment samples were taken from the bottom of aqua sources (in different depth) using the sediment sampler (model, Ekman grab) with package size 56x22x40cm [27].

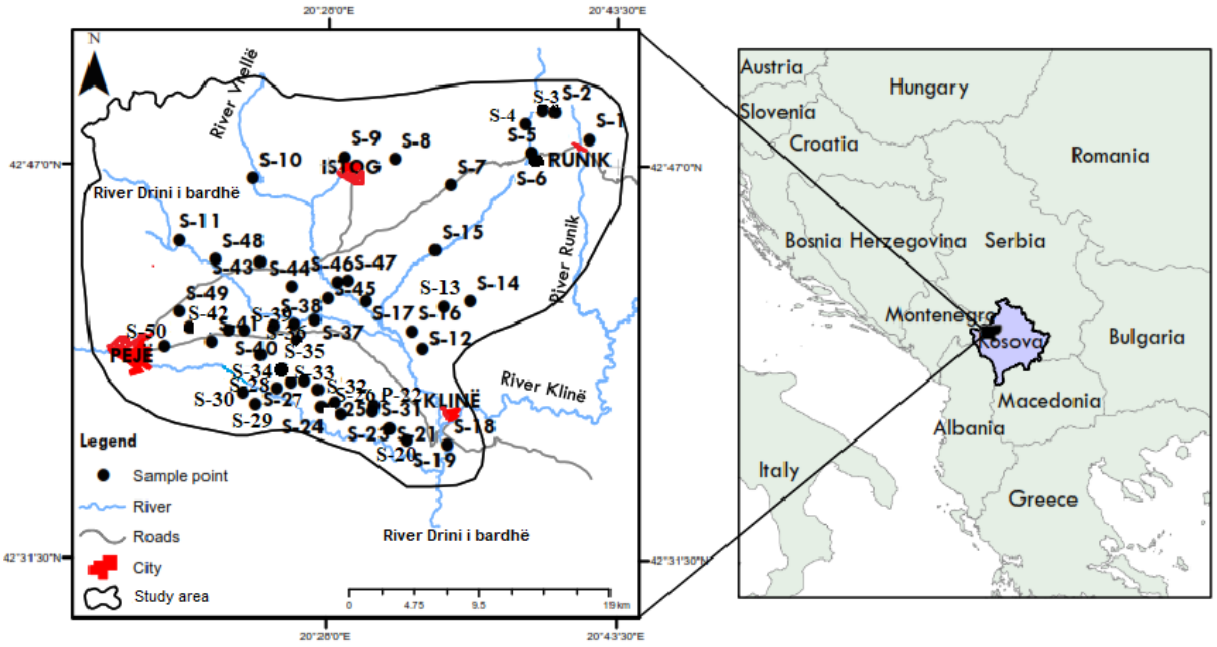

Figure 1. The study area with located sampling points.

According to the sampling procedure the sediment sampler was washed and dried with water before next sampling. Sampling material was collected at different sampling points, 1-2 kg of sediment, for the purpose of providing enough sediment fraction under 63 µm. Each sampling point has been coded and sampling material is collected in plastic bags and it is dried in the air for 21 days. Coarse materials were separated by using a sieve with 40 nm mesh, and afterwards sieve "Fritsch" with 63 µm was used for the separation purpose. Testing results are compared with the existing criteria for sediment quality given by SMSP, Falconbridge NC, SAS [28]. The locations of sampling points were determined by using the global positioning system (GPS) device, using a ''GARMIN'' GPS and such locations are described in details. The study area with the sampling point sections are shown in figure 1 and the details about sites are presented in table 1.

3.2. *Geochemical characterization of heavy metals in aquatic sediments*

The geochemical analysis of the aquatic sediment samples were performed at ''Actlabs'' laboratory in Canada by using "Ultratrace 2" testing program. Regarding to the declared standard operation procedure, the sample preparation procedure has started with 0.5 g of the aquatic sediment sample, under 63 µm, dissolved in aqua regia at 90º C in a microwave digestion unit and after that the prepared solution is diluted and analyzed with „Perkin Elmer SCIEX ELAN 6100" ICP-MS instrument. For the purpose of technical verification, the following reference materials (RM) were used: USGS GXR-1, GXR-2, GXR-4 and GXR-6. Mercury was determined using the same solution and the program 1G-Hg-CV was used as well as international standards SO-2, GXR-4, GXR2 and GXR-1. Testing laboratory procedure was done by using CV-AAS technique and the concentration was determined by using Hg vapor, with the reducing of Hg (II). In evaporating state it was used $SnCl_2$. Argon was run through the mixture of the sample for the purpose of reducing solution which transports the mercury atoms into adsorption cell situated in the beam (λ=253.7nm) of atomic adsorption spectrophotometer.

3.3. *Statistical assessment*

Basic 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 the program "Statistica 6" [29]. Multivariate statistics were used to assess the sources and distribution of heavy metals in natural aqua sediments in the study area. Outlier values are between 1.5 and 3 and extreme values are above 3. Principal component analysis (PCA) is considered the main of multivariate data analysis and it was firstly formulated by Pearson in statistics and after that it has been followed by Fisher and Mac Kenzie [30]. PCA was widely applied to reduce original variables of the contaminants and analyzing their sources. Statistical processing of chemical data and setting up the database, mainly for the purpose of achieving GIS maps, is an essential phase of sediment quality assessment. Cluster analysis of Q-mode was performed to find groups which contain similar sediment samples.

3.4. *Spatial distribution of heavy metals in sediments*

The GIS mapping methodology was applied to create geospatial distribution maps. The software "ArcView" version 10.1, was used for geospatial distribution mapping of analysed heavy metals in the study area [31].

Table 1. *Sampling stations, locality, coordinates and sea level with detailed locality description*

Sample	Locality	Coordinate X	Coordinate Y	Sea level (m)	Possible pollution sources
P1	Runik	427938	202933	721	Settlement, agriculture land
P2	Banjë e Runikut	424869	204008	766	Settlement, agriculture land
P3	Surigjan	4249112	2038904	680	Settlement, wastewater
P4	Cerkulez	4248422	2038347	684	Settlement, agriculture land
P5	Padalishtë	424731	203853	604	Settlement, agriculture land, wastewater
P6	Rakosh	4247316	203853	575	Settlement, agriculture land, wastewater
P7	Bellopojë	4246136	2034334	581	Settlement, agriculture land, wastewater
P8	Dubravë	4246754	2031355	549	Settlement, agriculture land
P9	Burimi - Istog	4274329	202886	560	Mountain tourism
P10	Burimi - Vrellë	424648	202397	509	Mountain tourism
P11	Radavc	4243635	2019644	593	Settlement, agriculture land
P12	Zllakuqan	4239467	2032678	439	Settlement, agriculture land
P13	Ranoc	4240855	2033738	466	Agriculture land, wastewater
P14	Leskoc	4241394	2034992	490	Settlement, agriculture land
P15	Osjan	4243409	2033467	493	Agriculture land, coal source
P16	Berkovë	4240275	2031954	438	Settlement, agriculture land
P17	Zabllaq	4241396	2029643	453	Settlement, agriculture land
P18	Gjurakovc	4242285	202905	477	Settlement, agriculture land
P19	Prekallë	4241837	2028288	485	Settlement, agriculture land
P20	Trubohovc	4241458	2027578	480	Settlement, agriculture land
P21	Staradran	4241751	2026059	492	Settlement, agriculture land
P22	Kashicë	4242709	2023831	515	Settlement, agriculture land
P23	Fusha e Pejës	4239513	2019206	525	Settlement, agriculture land
P24	Vitomiricë	4241141	2019667	549	Settlement, agriculture land
P25	Dubravë e Vogël	4243167	2022004	522	Settlement, agriculture land
P26	Klinë	423561	2034274	415	Agriculture land, wastewater
P27	Grabanicë	4235725	2032207	423	Settlement, agriculture land
P28	Drenoc	4236379	2031178	444	Settlement, agriculture land
P29	Poterq i ulët	4236373	2030825	431	Agriculture land, wastewater
P30	Poterq i epërm	423679	2030273	455	Agriculture land, wastewater
P31	Jabllanicë e Leshanit	4237089	2028447	446	Agriculture land, wastewater
P32	Kliqinë	4237292	2027433	448	Agriculture land, wastewater
P33	Leshan	4237685	2026971	463	Settlement, agriculture land
P34	Gllaviqicë	4238325	2026483	475	Settlement, agriculture land
P35	Gllaviqicë	4238287	202566	468	Settlement, agriculture land
P36	Vragoc	423774	2024783	490	Agriculture land, wastewater
P37	Millovanc	4237362	2024133	503	Settlement, agriculture land
P38	Gorozhdevc	4238014	2022916	506	Settlement, agriculture land
P39	Poterq	4236918	2029919	449	Settlement, agriculture land
P40	Jabllanicë	4237454	2028234	451	Agriculture land, wastewater
P41	Ramun	4238579	2024992	496	Settlement, agriculture land
P42	Llabjan	4239328	2024266	509	Agriculture land, Meat industry
P43	Lutogllavë	4239661	2025829	487	Agriculture land, garbage dump
P44	Ruhot	4240441	2026153	473	Settlement, agriculture land
P45	Terstenik	4240557	202722	460	Settlement, agriculture land
P46	Nabergjan	424041	2025084	489	Settlement, agriculture land
P47	Nabergjan i epërm	4240275	2023349	479	Settlement, agriculture land
P48	Nakull	423988	2022435	502	Settlement, agriculture land
P49	Bllagajë	424002	2021492	507	Agriculture land, wastewater
P50	Fusha e Pejës	423995	2020394	524	Settlement, agriculture land

4. Results

4.1. *Laboratory measurement techniques ICP-MS and CV-AAS*

Heavy metals in the aquatic sediment fractions, under 63µm, were determined by using ICP-MS and CV-AAS laboratory techniques, and results are presented in the table 2. The laboratory data were analyzed in randomized design and the limit of detection (LOD) for such metals is as follows: Fe 0.01 %, Mn 1 ppm, Co 0.1ppm, Cr 1ppm, Ni 0.1ppm, Cu 0.2ppm, Zn 0.1ppm, As 0.1ppm, Mo 0.01ppm, Ag 0.002ppm, Cd 0.01ppm, Pb 0.1ppm, Bi 0.02ppm, Sn 0.05ppm, Sb 0.02ppm and Hg 10 ppb.

4.2. *Statistical analysis*

The result of descriptive statistical analysis for heavy metals in 50 sediment samples (f<63µm) is presented in table 3. For each heavy metal, the values are given as arithmetic mean, geometric mean, median, minimal and maximal concentration, variance and standard deviation based on the total number of concentrations for every heavy metal. Comparision values, minimum and maximum, are done to assess the spreed of data. Using experimental data from table 2, frequency histograms and 2D scatter box with plots diagrams [32] for each heavy metal are presented in figures 2 and 3. The anomalous values (outliers and extremes) of heavy metals are presented in table 4. The relationship between the concentrations (mean values) of these heavy metals was shown by performing correlation analysis and Matrix for Pearson's correlation coefficients of selected variables and are displayed in table 5. The level of significance was set at $p < 0.05000$ for all statistical analyses. It was qualitatively assumed that the absolute values between 0.3 and 0.7, indicate good association, and those between 0.7 and 1.0 indicate strong association between elements. The clustering techniques (R and Q-mode) have often been applied to a wide variety of research issues [33-35]. Cluster analysis of R-mode (figure 4) has shown mutual links between studied heavy metals and observed that a heavy metal has the closest association with other heavy metals. Cluster analysis of Q-modality was performed on the total set of heavy metals presented in table 2. Sampling stations were grouped in 4 clusters and the results of Q-modality cluster analysis, with the distances given in parenthesis and means for each clasters, are presented in tables 6, 7 and 8.

4.3. *Geospatial distribution of heavy metals in sediments*

Geospatial distribution of of Fe, Mn, Co, Cr, Ni, Cu, Zn, As, Mo, Ag, Cd, Pb, Bi, Sn, Sb and Hg observed in 50 sediment samples are presented in figure 5.

Table 2. *Concetrations of 16 heavy metals in sediment (fraction <63 µm) of 50 aqua sources*. *****Limit of detection

Metal	Fe	Mn	Co	Cr	Ni	Cu	Zn	As	Mo	Ag	Cd	Pb	Bi	Sn	Sb	Hg
Unite	**%**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**ppb**
LOD*	**0.01**	**1**	**0.1**	**1**	**0.1**	**0.2**	**0.1**	**0.1**	**0.01**	**0.002**	**0.01**	**0.1**	**0.02**	**0.05**	**0.02**	**10**
P1	2.56	446	10.8	75	99.3	47.3	81.4	33.3	0.56	0.056	1.9	25.8	0.2	1.54	0.63	90
P2	8.7	391	14.5	53	88.3	85.6	1160	81.4	4.04	0.117	1.1	61.1	0.21	2.01	1.45	240
P3	2.07	723	10	27	33.2	25.8	83	8.7	0.64	0.052	0.38	33	0.19	0.74	0.88	70
P4	3.64	496	19.7	99	161	40.9	198	6.4	0.32	0.043	0.19	23.6	0.24	1.05	0.56	130
P5	2.75	645	25.3	101	184	32.7	76.6	6.3	0.38	0.037	0.22	17.4	0.25	0.64	0.38	80
P6	5.06	2500	28.2	52	69.4	75	85.2	10.4	0.68	0.021	0.07	48.9	0.36	0.86	0.52	40
P7	4.01	4360	24.5	37	68.9	132	92.6	14.8	0.86	0.074	0.29	33.1	0.48	0.78	0.95	150
P8	4.08	2480	25.4	45	69.6	114	104	23.9	0.86	0.043	0.24	30.1	0.47	1.06	1.51	240
P9	1.49	844	8.2	20	26.4	22	54.1	18.2	0.35	0.031	1.12	17.4	0.18	1.03	0.62	210
P10	2.23	6740	25	30	65.4	50.8	71.5	17.1	1.82	0.03	0.72	31.3	0.28	0.63	0.81	80
P11	3.65	2960	23.5	48	70.2	96.6	96	11.9	0.74	0.289	0.35	34	0.42	0.8	0.84	120
P12	2.83	990	20	85	157	42.4	105	6.8	0.42	3.89	0.28	22.4	0.21	1	0.4	80
P13	2.66	450	20.9	92	176	36.6	88.8	6.3	0.33	0.059	0.18	22.1	0.2	1.02	0.33	60
P14	2.71	755	21	88	160	42.5	169	11.1	0.4	0.074	0.26	32.2	0.37	1.05	0.56	140
P15	3.24	1450	22.4	81	152	41.9	93.7	10	0.44	0.068	0.32	34.1	0.27	0.99	0.56	70
P16	3.29	4100	25.1	56	94.8	88.2	169	11.9	0.51	0.12	0.62	37.4	0.42	2.52	0.86	180
P17	2.99	3530	23.2	57	90.1	84.2	190	10.8	0.5	0.142	0.59	40	0.43	1.91	0.83	190
P18	3.1	2050	17.6	58	80.3	60.8	128	9.3	0.43	0.075	0.33	28.5	0.38	1.34	0.61	110
P19	2.37	483	15.3	47	46.2	44.9	266	10.6	1.1	0.099	0.52	37.7	0.38	1.36	0.68	90
P20	2.99	1010	16	53	69.4	48.4	160	13.9	0.66	0.093	0.69	29.2	0.33	1.52	0.65	290
P21	2.8	973	17	62	77.2	41.7	142	9	0.61	0.063	0.53	30.3	0.31	1.02	0.6	110
P22	2.66	1770	16.3	57	59.9	35.3	79.8	27.6	0.41	0.07	0.28	44.5	0.35	1.45	0.81	40
P23	6.38	878	43.8	90	309	44.6	117	19.5	0.54	0.064	0.35	30	0.32	0.82	0.93	170
P24	2.82	2990	21	59	133	43.3	67.8	10.8	0.48	0.047	0.48	19.7	0.24	0.5	0.99	320
P25	11.9	996	108	89	559	44.9	184	18.5	0.45	0.055	0.18	30.8	0.3	0.56	0.83	200
P26	3.64	991	21.8	150	196	55.5	183	10.8	10.5	0.091	0.31	29.2	0.28	1.78	1.08	230
P27	2.51	316	14.4	62	108	34	459	7.2	0.41	0.084	0.29	31.2	0.24	0.98	0.61	160
P28	2.83	1800	18	47	67.8	56.9	124	9.4	0.59	0.059	0.39	28	0.33	0.86	0.59	90
P29	2.97	369	16.3	63	150	42.9	153	7.3	0.68	0.149	0.6	34.1	0.28	2.22	0.7	190
P30	2.64	499	14.6	65	130	101	720	7.6	0.45	0.413	0.63	64.1	0.38	2.84	0.75	350
P31	2.18	641	12.3	53	99.3	22.6	72.5	12.6	0.35	0.044	0.15	22	0.21	0.41	0.73	70
P32	2.66	885	17.3	60	124	35.1	91.9	9.5	0.43	0.087	0.3	28.3	0.28	0.72	0.77	90
P33	1.99	668	9.3	50	64.9	19.2	53.4	8.8	0.44	0.043	0.2	17.5	0.21	0.56	0.47	140
P34	4.05	395	14.9	54	79.3	34.3	79	12.1	0.52	0.052	0.06	22.1	0.36	0.86	1.07	40
P35	3.2	1710	17.2	53	92.5	53.2	411	12.7	0.52	0.11	0.31	39.9	0.3	1.5	0.69	100
P36	2.3	720	10.6	58	61.4	22	66.3	11	0.63	0.061	0.18	21.8	0.25	0.83	0.43	20
P37	2.44	526	19	81	131	23.1	71.1	5.3	0.2	0.059	0.17	19.2	0.23	0.41	0.27	140
P38	2.43	1020	13.9	58	78.1	29.1	180	7.7	0.37	0.06	0.37	29.5	0.23	0.95	0.39	140
P39	3.34	880	22.7	67	146	45.3	167	7	0.46	0.118	0.36	26.7	0.34	0.85	0.79	80
P40	12	807	25.2	119	156	341	306	15.2	5.17	1.84	0.53	73.7	0.43	44.7	1.74	370
P41	2.26	646	11.2	57	66.2	22.7	69.2	9.8	0.36	0.043	0.12	20.2	0.2	0.76	0.43	50
P42	12.8	541	13.8	42	41.4	26.2	3430	11.6	0.8	0.063	0.28	43.1	0.33	1.02	0.67	110
P43	2.51	505	12.6	43	67.4	37.7	89.6	4.6	0.29	0.045	0.22	19.5	0.23	1.31	0.59	140
P44	3.38	829	16.9	60	102	46	162	9.5	0.43	0.117	0.49	46.2	0.37	3.32	0.81	80
P45	3.22	2300	19.5	52	95.9	69.9	73.2	10.7	0.61	0.147	0.23	28.1	0.36	0.61	0.81	130
P46	2.45	756	12.5	53	75.8	35.6	154	10.1	1.1	0.067	0.7	85.5	0.38	3.48	1.23	40
P47	3.09	1520	17.9	49	110	33.9	82.5	10.8	0.34	0.069	0.33	30.7	0.3	0.64	0.83	70
P48	2.62	982	13.7	54	91.1	31.1	102	10.2	0.37	0.09	0.33	30.9	0.34	0.7	0.71	70
P49	2.98	1170	16.7	49	100	32.6	84.2	9.8	0.33	0.068	0.34	30.6	0.31	0.65	0.76	80
P50	2.73	450	12.8	52	85.3	36.3	97.4	10.1	0.51	0.106	0.32	33.9	0.34	0.89	0.72	190

Table 3. *Basic statistical analyses of 16 heavy metals in our study*

	Descriptive statistics						
Variable	**Mean**	**GeometricMedian**	**Minimum**	**Maximum**	**Variance**	**Std. Dev.**	
Fe /%	3.644	3.2134	2.8300	1.4900	12.800	6	2.467
Mn /ppm	1338.720	996.7633	879.0000	316.0000	6740.000	1564341	1250.736
Co /ppm	19.956	17.8767	17.2500	8.2000	108.000	199	14.112
Cr /ppm	62.240	58.5273	57.0000	20.0000	150.000	536	23.145
Ni /ppm	112.380	96.2778	91.8000	26.4000	559.000	6656	81.582
Cu /ppm	54.192	45.1774	42.4500	19.2000	341.000	2332	48.294
Zn /ppm	230.876	134.1354	103.0000	53.4000	3430.000	247316	497.309
As /ppm	12.998	11.1096	10.5000	4.6000	81.400	127	11.264
Mo /ppm	0.908	0.5826	0.4900	0.2000	10.500	3	1.626
Ag /ppm	0.196	0.0827	0.0680	0.0210	3.890	0	0.591
Cd /ppm	0.408	0.3325	0.3250	0.0600	1.900	0	0.309
Pb /ppm	33.012	30.8522	30.4500	17.4000	85.500	191	13.831
Bi /ppm	0.306	0.2961	0.3050	0.1800	0.480	0	0.078
Sn /ppm	2.041	1.1014	0.9850	0.4100	44.700	38	6.195
Sb /ppm	0.749	0.6996	0.7150	0.2700	1.740	0	0.290
Hg /ppb	133.400	111.3612	110.0000	20.0000	370.000	6668	81.657

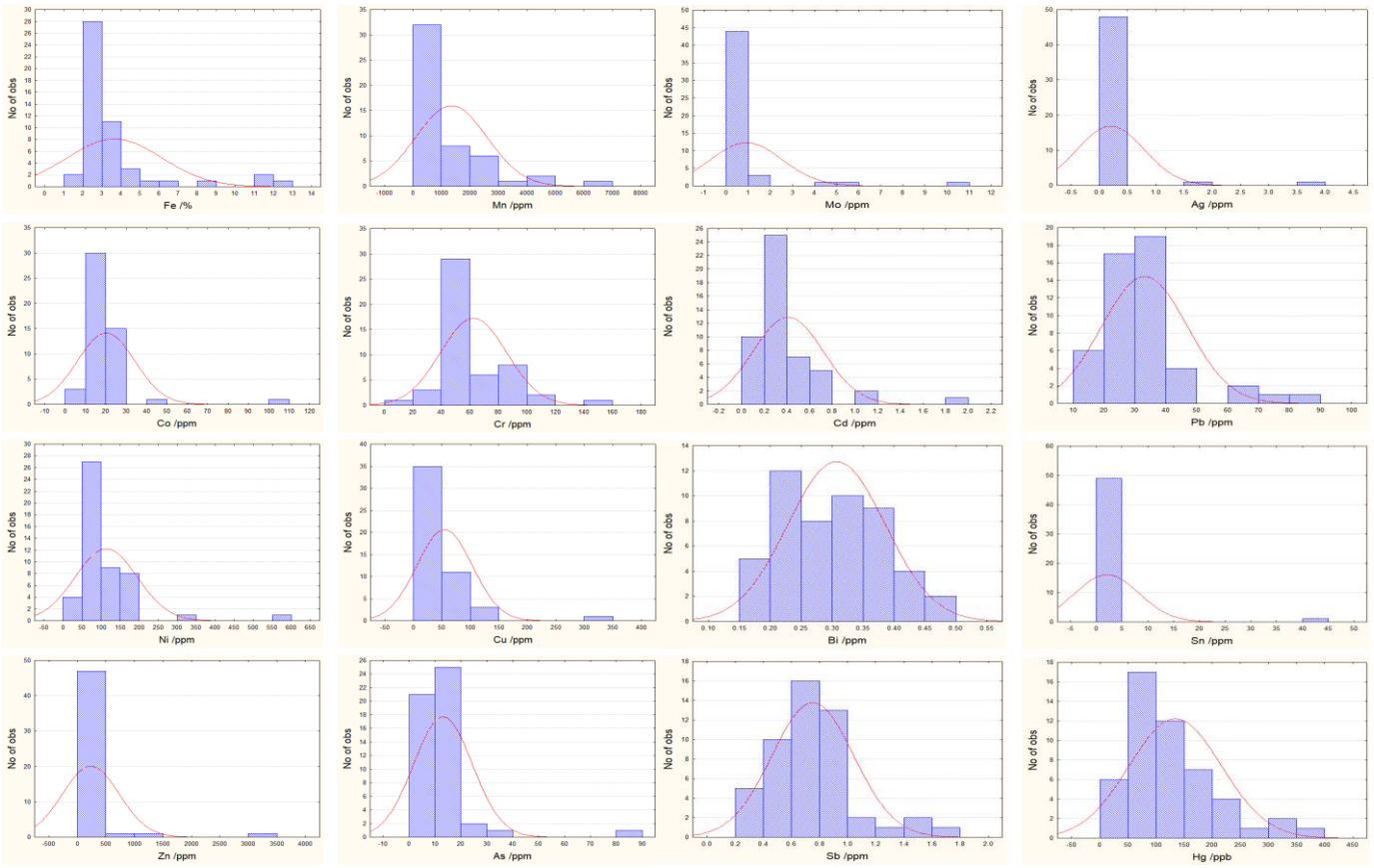

Figure 2. Frequency histograms of each measured heavy metal.

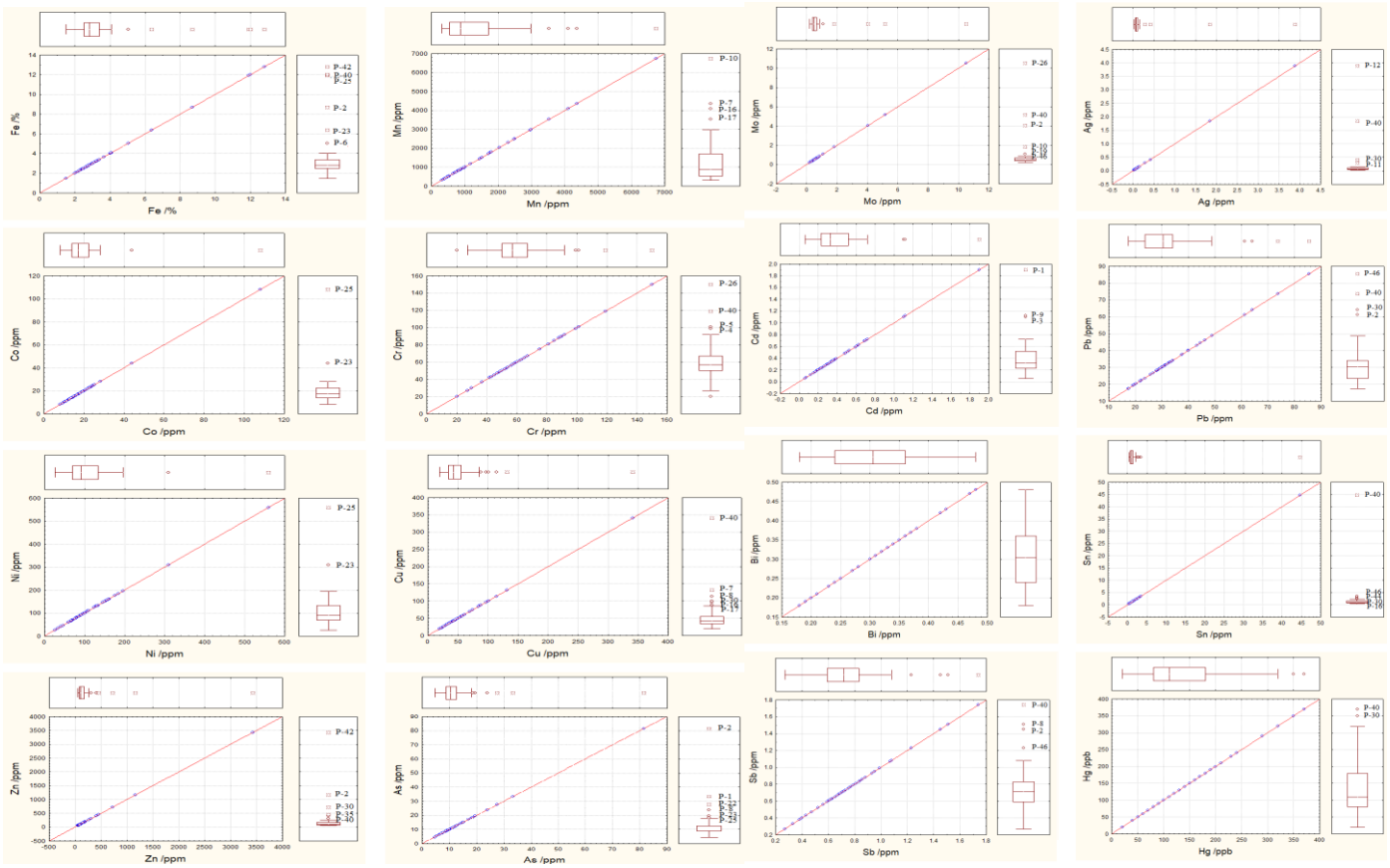

Figure 3. Scatterplot with plots diagrams of Fe, Mn, Co, Cr, Ni, Cu, Zn, As, Mo, Ag, Cd, Pb, Bi, Sn, Sb and Hg.

Table 4. *Sediment stations with anomalous values of heavy metals in sediments*

Sample station	Extreme values of heavy metals (¤)	Outlier values of heavy metals (o)
P1	As, Cd	
P2	Fe, Zn, Mo	Pb, Sb
P4	As	Cr, Cd
P5		Cr
P6		Fe
P7	Cu	Mn
P8		Cu, As, Sb
P9		Cd,
P10	Mn	Cu, Mo
P11		Ag
P12	Ag	
P16		Mn, Cu, Sn
P17		Mn, Cu
P19		Mo
P22	As	
P23	Fe	Co, Ni, As
P25	Fe, Co, Ni	As
P26	Cr, Mo	Cu
P30	Zn	Ag, Pb, Sn, Hg
P35	Zn	
P40	Fe, Cr, Cu, Mo, Ag, Pb, Sn, Sb	Zn, Hg
P42	Fe, Zn	
P44		Sn
P46	Mo, Pb	Sn, Sb

Table 5. *Matrix of Pearson's correlation coefficient*

Variable	Marked correlations are significant at p < 0.05000 N=16 (Casewise deletion of missing data)															
	Fe	**Mn**	**Co**	**Cr**	**Ni**	**Cu**	**Zn**	**As**	**Mo**	**Ag**	**Cd**	**Pb**	**Bi**	**Sn**	**Sb**	**Hg**
Fe	1.00	-0.08	0.54	0.26	0.45	0.49	0.61	0.35	0.30	0.16	-0.03	0.40	0.23	0.48	0.46	0.33
Mn	-0.08	1.00	0.15	-0.31	-0.15	0.23	-0.15	0.01	-0.00	-0.06	0.04	0.02	0.42	-0.07	0.18	0.03
Co	0.54	0.15	1.00	0.32	0.88	0.13	-0.07	0.05	0.02	0.02	-0.18	0.01	0.18	0.04	0.14	0.18
Cr	0.26	-0.31	0.32	1.00	0.61	0.26	-0.09	-0.09	0.55	0.28	-0.13	0.03	-0.07	0.36	0.05	0.23
Ni	0.45	-0.15	0.88	0.61	1.00	0.05	-0.10	-0.00	0.11	0.10	-0.16	-0.05	-0.06	0.06	0.05	0.21
Cu	0.49	0.23	0.13	0.26	0.05	1.00	0.02	0.17	0.40	0.35	0.12	0.53	0.54	0.87	0.65	0.55
Zn	0.61	-0.15	-0.07	-0.09	-0.10	0.02	1.00	0.22	0.10	-0.01	0.06	0.29	0.04	0.04	0.09	0.12
As	0.35	0.01	0.05	-0.09	-0.00	0.17	0.22	1.00	0.27	-0.06	0.52	0.30	-0.07	0.05	0.48	0.21
Mo	0.30	-0.00	0.02	0.55	0.11	0.40	0.10	0.27	1.00	0.12	0.12	0.28	0.05	0.40	0.50	0.36
Ag	0.16	-0.06	0.02	0.28	0.10	0.35	-0.01	-0.06	0.12	1.00	-0.02	0.12	-0.03	0.40	0.06	0.13
Cd	-0.03	0.04	-0.18	-0.13	-0.16	0.12	0.06	0.52	0.12	-0.02	1.00	0.25	-0.12	0.10	0.21	0.26
Pb	0.40	0.02	0.01	0.03	-0.05	0.53	0.29	0.30	0.28	0.12	0.25	1.00	0.47	0.50	0.58	0.25
Bi	0.23	0.42	0.18	-0.07	-0.06	0.54	0.04	-0.07	0.05	-0.03	-0.12	0.47	1.00	0.26	0.48	0.20
Sn	0.48	-0.07	0.04	0.36	0.06	0.87	0.04	0.05	0.40	0.40	0.10	0.50	0.26	1.00	0.52	0.44
Sb	0.46	0.18	0.14	0.05	0.05	0.65	0.09	0.48	0.50	0.06	0.21	0.58	0.48	0.52	1.00	0.47
Hg	0.33	0.03	0.18	0.23	0.21	0.55	0.12	0.21	0.36	0.13	0.26	0.25	0.20	0.44	0.47	1.00

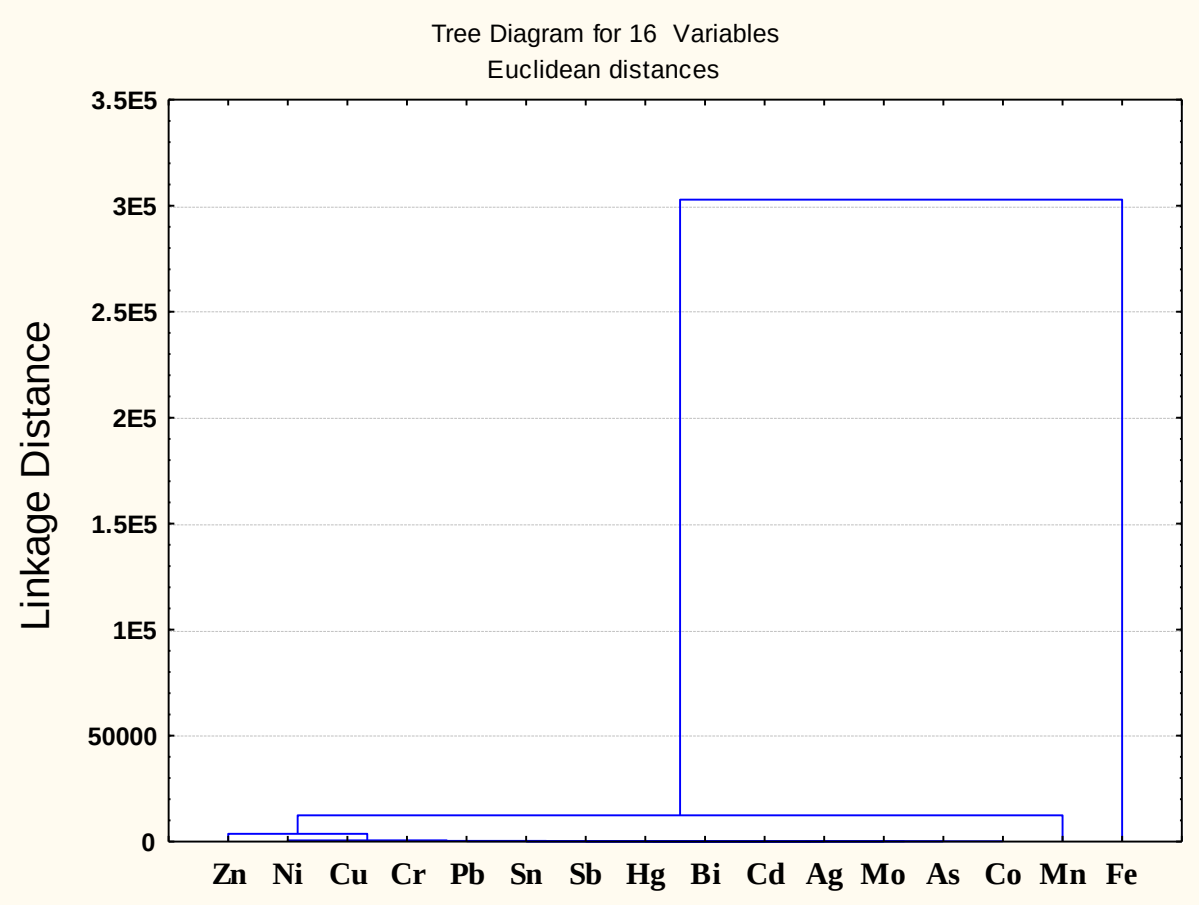

Figure 4. Three diagrams (claster analysis R mode) of heavy metals.

Table 6. *Members of 4 clusters and sample distances from respective cluster center*

Cluster	Sample (Euclidean distance)
Cluster 1	P2 (6625.558)
Members of cluster number 1	P25 (1406.674)
and distances from respective cluster center	P40 (1644.087)
Cluster contains 4 cases	P42 (3665.523)
Cluster 2	P6 (865.2656)
Members of cluster number 2	P7 (1851.607)
and distances from respective cluster center	P8 (1592.585)
Cluster contains 5 cases	P23 (4171.914)
	P34 (1720.182)
Cluster 3	P4 (1196.204)
Members of cluster number 3	P11 (1220.100)
and distances from respective cluster center	P12 (889.0694)
Cluster contains 18 cases	P15 (171.4548)
	P16 (655.6080)
	P17 (650.4109)
	P18 (210.4808)
	P20 (502.9491)
	P24 (948.4962)
	P26 (1170.644)
	P28 (869.7315)
	P29 (621.0716)
	P35 (86.67733)
	P39 (457.9894)
	P44 (553.5352)
	P45 (178.3801)
	P47 (226.3327)
	P49 (514.2028)
Cluster 4	P1 (338.3744)
Members of cluster number 4	P3 (916.5994)
and distances from respective cluster center	P5 (790.8154)
Cluster contains 23 cases	P9 (2364.552)
	P10 (1530.171)
	P13 (576.6923)
	P14 (688.3675)
	P19 (207.7841)
	P21 (910.8793)
	P22 (595.2787)
	P27 (260.6326)
	P30 (544.3116)
	P31 (644.8605)
	P32 (561.5455)
	P33 (1117.056)
	P36 (345.7798)
	P37 (115.1334)
	P38 (20.33507)
	P41 (447.2739)
	P43 (220.5822)
	P46 (67.18751)
	P48 (461.0017)
	P50 (747.6166)

Table 7. *Euclidean distances between 4 clusters*

	Euclidean distances between clusters Distances below diagonal Squared distances above diagonal			
Cluster number	**No. 1**	**No. 2**	**No. 3**	**No. 4**
No. 1	0.00	275278600	417555900	496745900
No. 2	16591.52	0.00	14798140	32582450
No. 3	20434.18	3847	0.00	3477830
No. 4	22287.80	5708	1865	0.00

Table 8. *Mean values of heavy metals in 4 clusters*

	Cluster Means			
Variable	**Cluster No. 1**	**Cluster No. 2**	**Cluster No. 3**	**Cluster No. 4**
Fe (ppm)	113500.0	47160.00	31777.78	24356.52
Mn (ppm)	683.8	2122.60	1730.28	975.78
Co (ppm)	40.4	27.36	19.75	14.96
Cr (ppm)	75.8	55.60	65.89	58.48
Ni (ppm)	211.2	119.24	114.89	91.74
Cu (ppm)	124.4	79.98	54.61	36.05
Zn (ppm)	1270.0	95.56	147.08	145.16
As (ppm)	31.7	16.14	9.99	11.42
Mo (ppm)	2.6	0.69	1.05	0.54
Ag (ppm)	0.5	0.05	0.32	0.08
Cd (ppm)	0.5	0.20	0.40	0.44
Pb (ppm)	52.2	32.84	31.24	31.10
Bi (ppm)	0.3	0.40	0.32	0.27
Sn (ppm)	12.1	0.88	1.34	1.10
Sb (ppm)	1.2	1.00	0.74	0.63
Hg (ppm)	0.2	0.13	0.14	0.11

5. Discussion

5.1. *Discussion of ICP-MS and CV-AAS analyses and toxicity*

Results from the chemical data (see table 2) can be used for the assessment of sediment quality and contamination by toxic elements. Concentrations of each heavy metal were used to compare the obtained amounts of the selected toxic elements with the existing criteria for sediment quality by SMSP, SAS. According to the study findings, in all sampling points, Fe ranged 1.49-12.8 % with the mean value of 3.644 %. Comparative analysis showed that Iron in six points (P2, P6, P23, P25, P40 and P42) exceed recommended norms from 4.38 % (causing significant toxic effects and making aquatic life unsuitable). The high concentration is probably due to natural and geological factors because Fe is richly present in the earth's crust. The highest value of Iron, 12.8 %, was measured at sample station number P42. Based on the building constuction zone there is a meat factory object that might have significant influence for such level of iron concentration. The concentrations of Mn ranged 316-6740 ppm with the mean value from 1338.72 ppm. Using comparative analysis, Manganese in 16 points exceeded recommended norms from 1100 ppm (causing significant toxic effects) and the highest value of 6740 ppm was measured at sample point P10 as sign of rock composition in that area and also as a possibility of using fertilizers, varnish and fungicides and livestock feeding supplements. Mn concentration ranged from 316-6740 ppm with the mean value from 1338.72 ppm. Using comparative analysis, Manganese in 16 points exceeded recommended norms from 1100 ppm (causing significant toxic effects) and the highest value of 6740 ppm was measured at sample point P10 as sign of rock composition in that area and as a possibility of using fertilizers, varnish and fungicides and livestock feeding supplements [36].

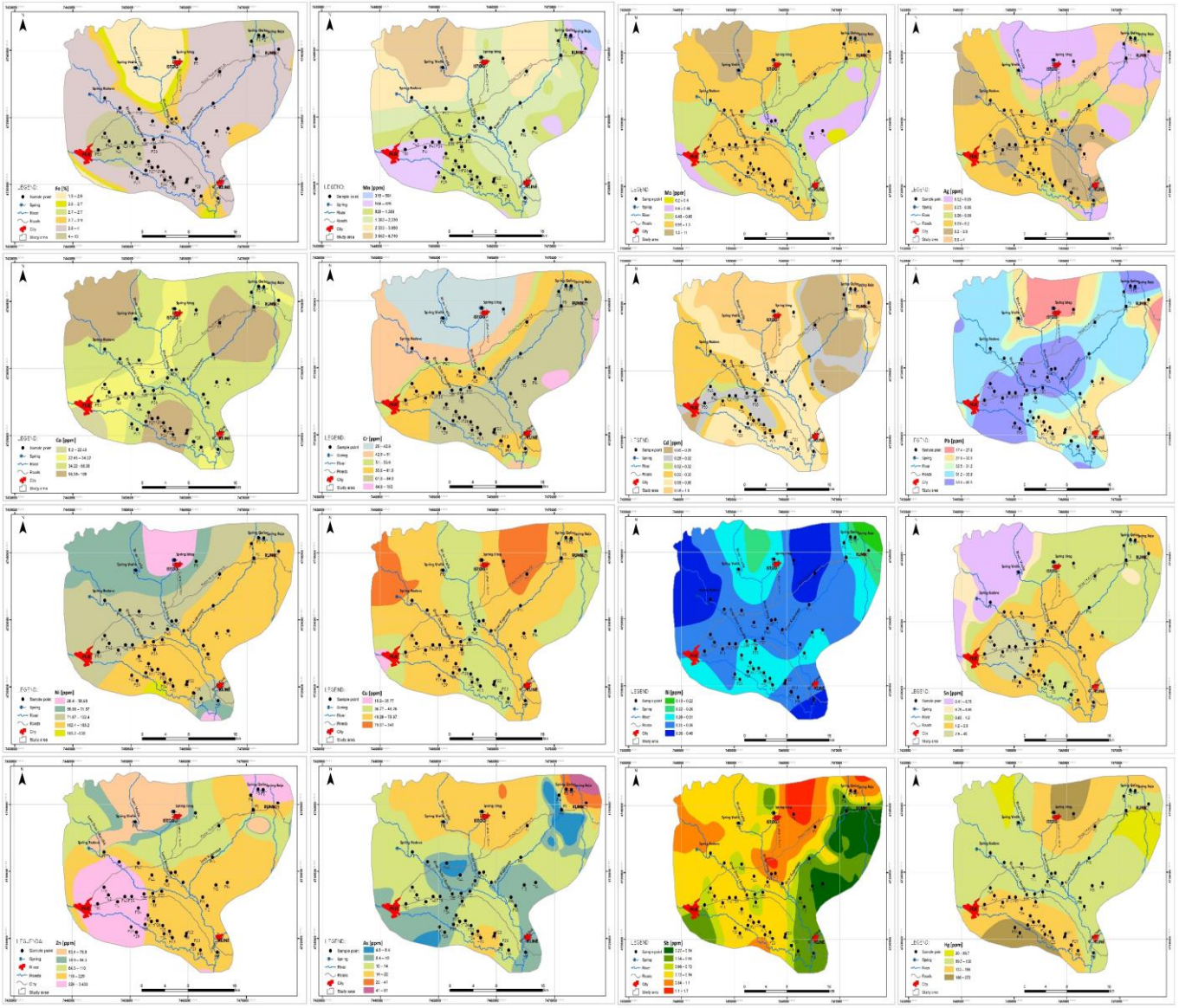

Figure 5. Geospatial distribution maps in the study area.

Concentrations value of Co (except sample P25) in all samples were lower than recommended norms from 50 ppm and ranged between 8.2-108 ppm with the mean value from 19.956 ppm. The highest value of 108 ppm was measured at sample point P25 as sign of rock composition in the form of arsenides and sulphides minerals of cobaltite (CoAsS), linnaet (Co_3S_4), smaltyn ($CoAs_2$) and karrolit ($CuCo_2S_4$). The concentration of Cr (except points P26 and P40) in all samples were lower than recommended norms from 110 ppm and ranged 20-150 ppm with the mean value from 19.956 ppm. The highest value of 150 ppm was measured at sample point P26 as sign of rock composition in form of chromate mineral ($FeCr_2O_4$), which contains up to 70% of pure Cr_2O_3. The higher content of such element in the environment is caused by human activity. According to the concentration of Ni, in all sampling points it ranged between 26.4-559 ppm with the mean value of 112.38 ppm. Our comparative analysis shows that Nickel in 34 points exceeded recommended norms from 75 ppm (causing significant toxic effects). The high concentration of Ni in this area might be as a sign of rock Ni-mineral most as magnesium - iron silicates [37]. Cu level ranged 19.2-341 ppm with the mean value from 54.192 ppm. Excluded sample points P6, P7 and P40, in all other samples there were lower concentration compared to the recommended norms from 110 ppm. The hight value of Cuprum in sediments come from using of Copper compounds as fungicides, algaecides and insecticides in this area [38]. The concentration

value of Zn below 90 ppm, represents non-contaminated sediments. Zn is founded to be in the range between 53.4-3430 ppm, with the mean value from 230.88 ppm. The highest value, 3430 ppm, was measured at sample point P42. Comparative analysis of Zn levels showed that seven points (P2, P19, P27, P30, P35, P40 and P42) exceed recommended norms from 200 ppm (causing significant toxic effects and making aquatic life unsuitable). Concentration value of As (except points P1 and P2) in all samples is lower than recommended norms from 33 ppm with the mean value from 12.998 ppm. The highest value of 81.4 ppm was measured at sample point P2 as sign of rock composition in the form of As minerals. Concentration value of Mo (except points P2, P26 and P40) in all samples were lower than recommended norms from 4 ppm. Mo ranged between 0.2-10.5 ppm with the mean value from 0.908 ppm. The highest value is reached at sample point P26. Ag ranged 0.021-3.89 ppm with the mean value from 0.196 ppm and the highest value was measured at sample point P12. Excluded sample points number P12 and P40, in all other samples the concentration value of Ag were lower than recommended norms from 0.5 ppm. The concentration of the heavy metals Bi and Sn are in ranges between 0.18-0.48 ppm, 0.41-44.7 ppm respectively. The concentration value of Cd, Pb, Sb and Hg in all sampling points are under the value of significant toxic effects for each heavy metal. Sediments contaminated with Cd lower than 10 ppm, Pb lower than 2 ppm, Sb lower than 500 ppm and Hg lower than 2 ppm are classified as non-contaminated areas. Cd is ranged between 0.06-1.9 ppm with mean from 0.408 ppm. Pb was ranged 17.4-85.5 ppm with mean from 33.012 ppm, Sb was ranged 0.27-1.74 ppm with mean from 0.75 ppm. Hg was ranged 20-370 ppb with mean from 133.4 ppb.

Based on the laboratory results the concentration values shows that the mean value of every heavy metal, in the sediments of aqua sources, follows such trend: Fe > Mn > Zn > Ni > Cr > Cu > Pb > Co > As > Sn > Mo > Sb > Cd > Bi > Ag > Hg.

5.2. ***Statistical interpretation***

The descriptive statistics of 16 heavy metals in the sediment fraction, under 63 mμ, 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 the table 2 and box plot approach, anomalous values (extreme and outlier) of all analyzed heavy metals were determined. Also Frequency histograms and 2D Scatter box plot diagrams for the measured heavy metals are presented in figures 2 and 3.

Analyzing the Frequency histograms and Scatter box plot diagrams, extreme and outlier values of measured heavy metals were defined and presented in table 4. Correlation Pearson's factor was calculated to see if some of the parameters are interrelated with each other and the results are presented in table 5. Regarding to the correlation analyses, Co shows high significant positive relationship with Ni, Cu shows high significant positive relationship with Sn and Sb, and finally Zn shows high significant positive relationship with Fe. Cluster analysis (R- and Q-mode) is another type of classification for the sample points in terms of their similarities or differences. Cluster analysis of R-mode presented in figure 3, shows mutual links between studied variables and it could be observed that Fe has the closest association with Mn. After that, Mn has the clossest with Zn and they form one branch of the dendogram linked with the other one, in which Ni, Cu, Cr, Pb, Sn, Sb, Hg, Bi, Cd, Ag, Mo, As and Co follows. These correlations are highlighted, suggesting similar sources and similar geochemical processes that could control the occurrence of these heavy metals in analysed aquatic sediments. Cluster analysis of Q-modality was performed on the total set of geochemical data from table 2 and samples were grouped in 4 clusters and results of Q-modality cluster analysis, with the Euclidian distance and means of metal of each clusters are given in parenthesis (tables 6, 7 and 8). In case of 4 clusters, the cluster 1 is composed by 4 sediment samples, the cluster 2 is composed by 5 sediment samples, the cluster 3 is composed by 18 sediment samples and the cluster 4 is a composition of 23 sediment samples.

5.3. ***Geospatial distribution of heavy metals in sediments***

Geospatial distribution maps of heavy metals (Fe, Mn, Co, Cr, Ni, Cu, Zn, As, Mo, Ag, Cd, Pb, Bi, Sn, Sb and Hg) are presented in figure 5, and they show high concentration values in different parts of the study area. By analyzing the created maps, the high concentrations of some metals are located mostly in the north-east, north-west and south-west part of the catchment basin. The highest measured concentrations of some heavy metals were detected in sediment samples points: P1, P2, P4-P12, P16, P17, P22, P23, P25, P26, P30, P35, P40, P42 and P46. The exceeded mass concentrations for some heavy metals in sediment, in this area, were directly impacted from the geological constitution of rocks: clastic, alluvium, proluvium, glacigene, calc tufa/travertine and lake sediments [39] and by the influence of human activity (case of Iron impacted from of Meat factory).

6. Conclusion

Geochemical, geospatial and statistical analyses of the sediments (fraction <63 μm) in water sources of Drini i Bardhë river basin have been widely described. For better understanding of geochemical consistence of aqua sediments, ICP-MS and CV-AAS laboratory techniques were used. In terms of statistical interpretation, the mean concentration of the studied heavy metals have decreased in such ranking:

Fe>Mn>Zn>Ni>Cr>Cu>Pb>Co>As>Sn>Mo>Sb>Cd>Bi>Ag>Hg. Regarding to the correlation analyses, Co shows high significant positive relationship with Ni. Cu shows high significant positive relationship with Sn and Sb, and finally Zn shows high significant positive relationship with Fe. Cluster analysis of R-mode (the dendogram) shows that Fe has the closest association with Mn. Mn has the clossest association with Zn and they form one branch of the dendogram linked with the other one, in which Ni, Cu, Cr, Pb, Sn, Sb, Hg, Bi, Cd, Ag, Mo, As and followed by Co. These correlations between these heavy metals are highlighted, suggesting similar sources and similar geochemical processes that could control the occurrence of these heavy metals in analysed aquatic sediments. By analyzing the geospatial distribution maps, the high concentrations of some metals are located mostly in the north-east, north-west and south-west part of the catchment basin. By comparing the concentrations of heavy metals in sediment with the existing criteria, it was found out that sample points P1, P2, P4-P12, P16, P17, P22, P23, P25, P26, P30, P35, P40, P42 and P46 are significantly polluted and exceeded mass concentrations of some heavy metals in sediment, with directly impact from the geological constitution of rocks and with a minor influence by human activity, the case of iron concentration by the meat factory activities. The authors suggestions are to keep and develop sediment monitoring programs in the near future and this study will be a useful tool for the local authorities who has responsibility for the natural resources in Kosovo.

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