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HEAVY METALS IN SEDIMENTS FROM THE FANI AND MATI RIVERS (ALBANIA)

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Abstract Scientific information on affecting degree by heavy metals of sediments from Fani and Mati rivers (northern Albania) is limited. In this study, the sediment samples taken from these rivers, and ore and calcine samples taken from the industrial sites located within the basins of these rivers were analyzed by atomic absorption spectrometry for Cd, Pb, Zn, Cu, Cr, As and Ni, to determine the enrichment of these elements. The results indicated that the sediment samples contained up to 736 mg/kg Ni, 618 mg/kg Zn, 26.1 mg/kg Pb, 0.83 mg/kg Cd, 1167 mg/kg Cu, 408.7 mg/kg As, and 375.8 mg/kg Cr. The highest metal concentrations are found in sediments collected below the Rubiku and Kurbneshi sites. Although the data exhibited significant dilution of some heavy metals in sediments from downstream, the concentrations of Cr, Ni, Zn and Cd exceed the values at the 90th percentile, while the concentrations of Cu and As exceed the maximum values (Geochemical Atlas of Europe). The ore and calcine leachates contained up to 16800 mg/kg Cu, 53 mg/kg Ni, 81 mg/kg Zn and 0.31 mg/kg Cd, suggesting that the existing wastes contain soluble copper, zinc, nickel and cadmium. The risk of heavy metals in the environment is high because of the elevated levels of Cr, Ni, Cu, Zn, As and Cd in the river sediments. The results indicate downstream transference of these metals from the studied sites.

Key words: Fani-Mati rivers system; heavy metals; pollution; river sediments; Albania

1. INTRODUCTION

The distribution of heavy metals in soils and sediments in Albania has made them high priority pollutants at national level. Many researches in last decade have focused on pollution of soils and sediments by these elements derived from industrial activities (Beqiraj et al., 2008; Gjoka et al., 2007; Çullaj et al., 2000). Until 1990, mining and processing of copper were among the important industrial activities in Albania. Extraction of copper ore during the period 1986-1996 was about 6,800,000 tones, and the accumulated wastes from the Cu-industry were 23.8 Million m^3 (Ministry of Environment, Forestry and Water Administration, 2006). Actually, the copper industry in Albania is not operating. The mines were closed, while factories were abandoned and destroyed.

A lot of copper mines and factories are found in the mining area of Mirdita, within the basins of Fani and Mati rivers, in which the cumulative production of mines was about 350kt/year making this area one of the highest production zones in the country. Due to the arsenopyrites nature of the ores, significant concentrations of arsenic are among the heavy metals in effluents. High content of pyrite in ore and waste increase their capacity to release heavy metals (Gray, 2003).

However, of great importance from the environmental point of view are the four copper sites, Spaçi Cu-mine, Repsi Cu-enrichment factory, Kurbneshi Cu-enrichment factory and Rubiku Cu-plant, because they are the major sources of air, soil and water pollution in the area. Significant stockpiles of calcine, concentrate and unprocessed ore were found at these sites, especially at Rubiku Cu-plant. This plant, during more productive years, generated approximately 30000 tons of mineral residues annually (UNEP, 2000). Therefore, presence of these copper sites is a potential risk to local communities and aquatic systems when drainage from these sites enters streams and rivers. At the moment, in Albania there are no laws regarding permissible concentrations of heavy metals in sediments.

The purpose of this study was to analyze heavy metal (Cd, Cr, Ni, Pb, Zn, Cu and As) concentrations found in sediments of Fani and Mati Rivers that are subjected to point pollution sources, in order to evaluate the pollution levels of these sediments by heavy metals and determine the potential of ore and calcine samples to generate heavy metals.

2. MATERIALS AND METHODS

2.1 The study area

The study area is located in the District of Mirdita (northern Albania). The study comprised the most important mining and metals processing sites in this area, which were within the Fani-Mati Rivers system (Fig. 1). The Cu-mine in Spaç is adjacent to Spaçi Stream, the Cu-enrichment factory in Reps is adjacent to Fani i Vogel River, the Cu-enrichment factory in Kurbnesh is adjacent to Uraka River and Cu-plant in Rubik is adjacent to Fani River.

The Spaci Stream flows into the Fani i Vogel River, a main tributary to the Fani River which flows into the Mati River, and the Uraka River flows into the Mati River (final recipient) that discharges into the Adriatic Sea

There are a number of environmental concerns associated with effluents from these sites, including tailings deposited directly adjacent to riverbeds: contamination with heavy metals (like Cu, Zn, As, Ni and Cr) of land, surface, ground and river waters downstream of the sites, and air pollution.

Geologically, the Jurassic and Triassic magmatic rocks, Neogene sand- and siltstones, and Cretaceous limestone dominate the study area (Fig. 2). The Quaternary deposits (gravel) are of limited occurrence. The high Cu, Ni, As and other elements concentrations in sediment samples could also be attributed to erosion of these magmatic rocks and successive transport towards the riverbeds of the eroded materials.

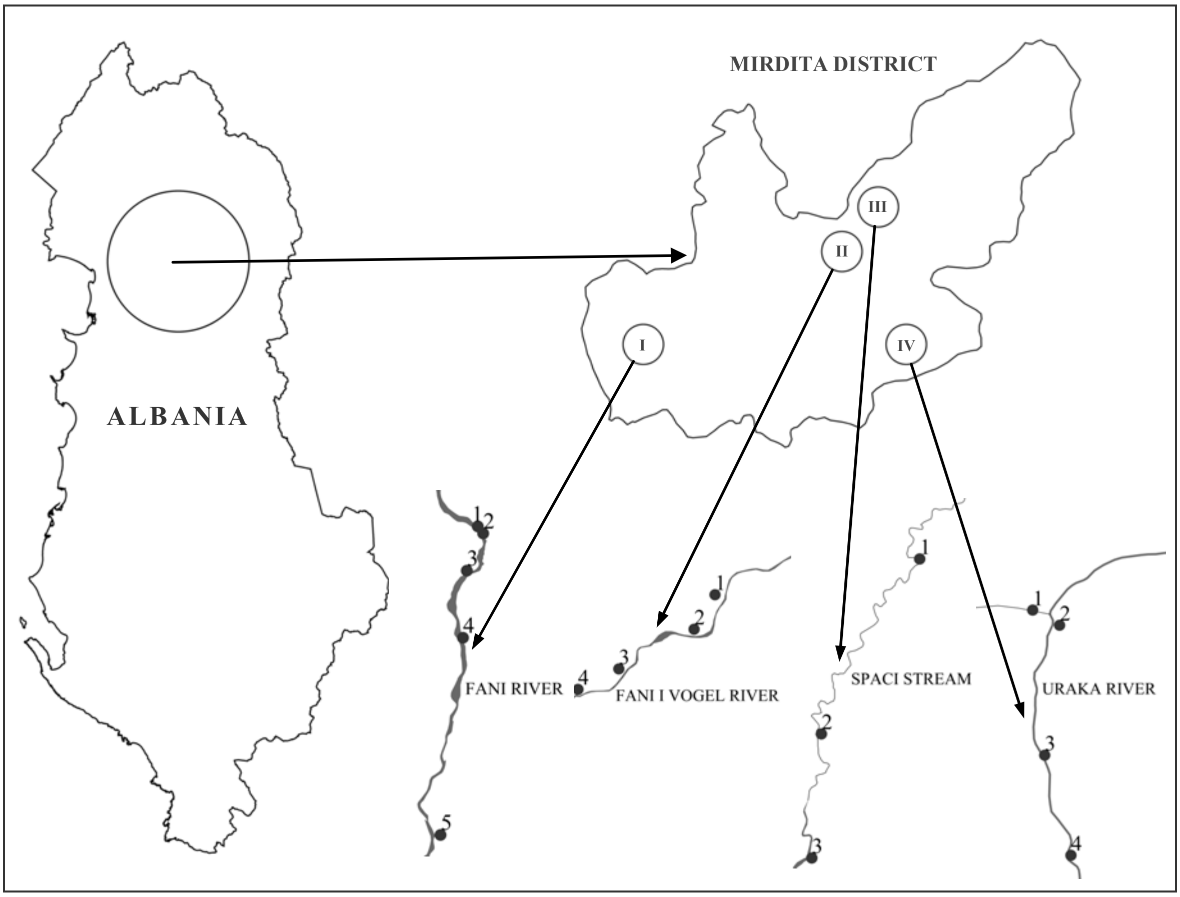

Figure 1. Study area and sampling points: I – Rubik ($RuSP_1$, $RuSP_2$, $RuSP_3$, $RuSP_4$, $RuSP_5$); II – Reps ($RuSP_1$, $RuSP_2$, $RuSP_3$, $RuSP_4$); III – Spac ($RuSP_1$, $RuSP_2$, $RuSP_3$); IV – Kurbnesh ($RuSP_1$, $RuSP_2$, $RuSP_3$, $RuSP_4$).

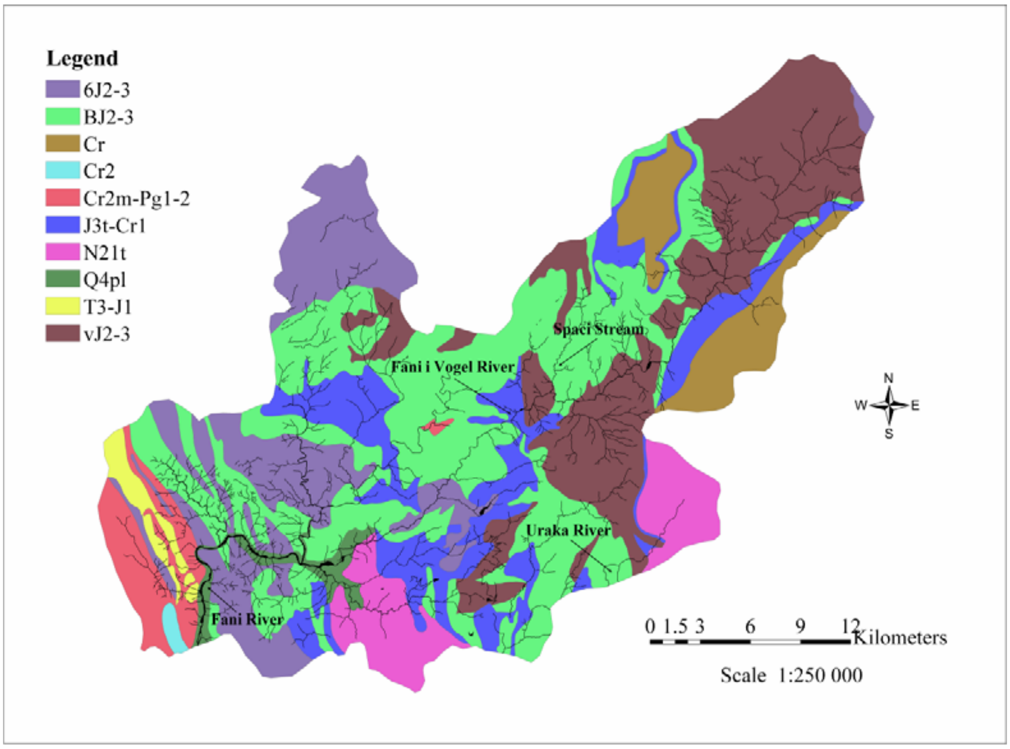

Figure 2. Geological map of the study area.

Legend: 6J2-3 - Ultrabasic intrusive rocks; BJ2-3 - Basic and intermediate effusive rocks and pyroclastites; Cr - Stratified and massive limestones, generally strongly karstified; Cr2 - Stratified limestones, joined; Cr2m-Pg1-2 - Siltstones, sandstones, marlstones, subordinately limestones (flysch); J3t-Cr1 - Sandstones, marlstones, conglomerates, shales and gravels of variable grain size; N21t - Limestones, conglomerates, sandstones and siltstones; Q4pl - Gravel to sands, boulders; T3-J1 - Limestones, limestones with siliceous rocks, dolomites, joined and strongly karstified; vJ2-3 - Basic intrusive rocks.

2.2 Sample collection and preparation

Ore and calcine samples were collected from the copper mine and factories for water-leaching studies to evaluate their potential to release heavy metals and to estimate the amount of these elements remaining in the ore and calcine piles. River sediment samples were collected at several sampling points (SP) for each the studied site (3 SP from Sefa Stream in Spac; 4 SP from Fani Vogel River in Reps; 4 SP from Uraka River in Kurbnesh; and 5 SP from Fani River in Rubik) on June 2008 to evaluate distribution of heavy metals in and around the respective sites. Sediment samples consisted of bed alluvium. The ores calcines and sediments collected were composite samples. All samples were stored in polyethylene bags. Sediment samples after air-drying were passed through a plastic sieve with a 2-mm mesh. Finely ground samples were prepared by grinding a sub-sample of about 50-60 g of < 2-mm soil to a fine powder in a special mill. Ore and calcines samples were air-dried and sieved to 9.5 mm prior to leaching. Then, 50 g of sample were leached with 1 l of deionized water acidified to pH 4.2, and rotated at 28 rpm for 18 h. The leachates were filtered at 0.45-µm.

2.3 Analytical procedure

The sediment, ore and calcine samples were analyzed for total concentrations of Cd, Cr, Ni, Pb, Zn, Cu and As. The sediment samples were also analyzed for pH, $CaCO_3$, and for total carbon, nitrogen and sulfur. The ore and calcine leachate samples were analyzed for Cd, Cr, Ni, Pb, Zn, Cu, As and SO_4 and for conductivity and pH. The sediment pH was measured in a 2.5:1 0.01 M $CaCl_2$ solution: sediment ratio by pH-meter, after DIN ISO 10390; carbonates content by calcimeter, following DIN 18129; total carbon, nitrogen and sulfur contents by the gas-chromatography using a C-N-S element analyzer (Heraeus). Leachate pH and conductivity were measured by pH-meter and Conductivity-meter, respectively. Heavy metals and sulphate in leachate samples and heavy metals in sediment, concentrate and calcine samples (at aqua-regia extract) were determined by atomic absorption spectrometer (AAS), following DIN ISO 11466. Element concentrations in the extracts were determined by the atomic adsorption spectrometer FAAS 4100 (Perkin Elmer). The accuracy of the method was confirmed by analyzing the certified reference materials and the recovery studies.

2.4 Data analysis

Metal concentrations are presented on a dry weight basis (mg/kg dry weight). All the obtained data were subjected to statistical analysis using the SPSS 16.0 for Windows. For all statistical analyses, $p<0.05$ was considered significant. Correlation is widely used in heavy metal analyses to explain their origin and mechanisms of deposition in the sediments as well as to evaluate the potential of the concentrate or calcines to leach heavy metals.

3. RESULTS AND DISCUSSION

3.1 Chemical properties of sediment

The chemical properties of sediment samples used in this study are presented in Table 1. Generally, pH values increased with distance from the copper sites. The pH in sediments of Sefa Stream (Spaci, at three sampling points) and Uraka River (Kurbneshi, at KuSP1 and KuSP2) was strongly acid. This is mostly attributable to discharge of acid effluents from the Cu-mine and Cu-enrichment factory to these sites. At acid conditions, all the analyzed metals, except Cr, could be desorbed from the sediment. While the pH values in sediments from other sampling sites were neutral. The trend of carbonates was just similar to pH. A significant correlation occurred between pH and $CaCO_3$ ($r=0.74$, $p<0.01$). The highest organic carbon contents in sediments collected 100m below the Rubik site (RuSP2) and 5km below the Reps site (ReSP5) suggest the inflow of organic wastes from the residences.

3.2 Total concentrations of heavy metal in sediment

Metal concentrations in sediment samples are shown in Table 2. River sediment samples collected within 100m of the copper sites contain: (i) for the Spaçi site, 589 mg/kg Cu, 229 mg/kg Zn, 0.3 mg/kg Cd, 49,7 mg/kg As, 77 mg/kg Cr and 25 mg/kg Ni; (ii) for the Repsi site, 262 mg/kg Cu, 178 mg/kg Zn, 0.2 mg/kg Cd, 15.1 mg/kg As, 242 mg/kg Cr and 111 mg/kg Ni; (iii) for the Kurbneshi site, 1167 mg/kg Cu, 118 mg/kg Zn, 0.13 mg/kg Cd, 408.7 mg/kg As, 354 mg/kg Cr and 50 mg/kg Ni; and (iv) for the Rubiku site, 761 mg/kg Cu, 272 mg/kg Zn, 0.71 mg/kg Cd, 28.84 mg/kg As, 269 mg/kg Cr and 391 mg/kg Ni.

While, sediments samples collected 5 km from these sites contain: (i) for the Spaçi site, 490 mg/kg Cu, 156 mg/kg Zn, 0.2 mg/kg Cd, 14.6 mg/kg As, 63 mg/kg Cr and 26 mg/kg Ni; (ii) for the Repsi site, 289 mg/kg Cu, 322 mg/kg Zn, 0.3 mg/kg Cd, 16.7 mg/kg As, 110 mg/kg Cr and 119 mg/kg Ni; (iii) for the Kurbneshi site, (2 km) 652 mg/kg Cu, 152 mg/kg Zn, 0.23 mg/kg Cd, 150.8 mg/kg As, 320 mg/kg Cr and 240 mg/kg Ni; and (iv) for the Rubiku site, 200 mg/kg Cu, 198 mg/kg Zn, 0.26 mg/kg Cd, 9.6 mg/kg As, 264 mg/kg Cr and 394 mg/kg Ni.

Table 1. Chemical properties of sediment samples collected in this study*

Location/description	*pH $CaCl_2$*	*$CaCO_3$*	*C_{tot}*	*C_{org}*	*N_{tot}*	*S_{tot}*
		(%)				
Rubik Cu Plant, stream sediment close to plant	7.05	2.10	0.996	0.746	0.111	0.450
Rubik Cu Plant, stream sediment 100m below plant	7.06	0.43	2.809	2.759	0.292	0.540
Rubik Cu Plant, stream sediment 1 km below plant	7.27	3.44	1.181	0.771	0.127	0.258
Rubik Cu Plant, stream sediment 2 km below plant	7.22	1.03	1.307	1.187	0.123	0.137
Rubik Cu Plant, stream sediment 5 km below plant	7.29	2.48	1.382	1.085	0.108	0.217
Spaç Cu mine, stream sediment close to mine	4.04	0.05	0.973	0.967	0.057	0.852
Spaç Cu mine, stream sediment 2 km below mine	4.01	0.05	0.206	0.2	0.015	0.278
Spaç Cu mine, stream sediment 5 km below mine	4.09	0.03	0.366	0.363	0.025	0.299
Reps Cu factory, stream sediment 100m below factory	6.73	1.11	0.475	0.345	0.035	0.148
Reps Cu factory, stream sediment 1 km below factory	7.02	3.44	1.322	0.912	0.073	0.264
Reps Cu factory, stream sediment 2 km below factory	7.17	2.40	0.609	0.319	0.033	0.144
Reps Cu factory, stream sediment 5 km below factory	7.27	4.40	3.200	2.67	0.138	0.148
Kurbnesh Cu factory, stream sediment closed to factory	3.46	0.00	0.312	0.312	0.032	1.680
Kurbnesh Cu factory, stream sediment 100m below factory	3.30	0.00	0.395	0.395	0.042	2.062
Kurbnesh Cu factory, stream sediment 1 km below factory	6.59	0.76	0.596	0.506	0.049	2.175
Kurbnesh Cu factory, stream sediment 2 km below factory	6.84	2.01	0.933	0.693	0.060	0.563
Mean	5.96	1.44	1.1	0.90	0.08	0.65
Median	6.84	1.03	0.9	0.69	0.06	0.28
Standard Deviation	1.62	1.48	0.9	0.80	0.07	0.72
Minimum	3.30	0.00	0.2	0.20	0.02	0.14
Maximum	7.29	4.40	3.20	2.76	0.29	2.18

*Confidence Level (95.0%)

Table 2. Concentrations of heavy metals in sediment samples (mg/kg of dry weight) collected in this study*

Location/description	*Cr*	*Ni*	*Cu*	*Zn*	*Pb*	*Cd*	*As*
Rubik Cu Plant, stream sediment close to plant	158	157	846	618	23,0	0.827	23.270
Rubik Cu Plant, stream sediment 100 m below plant	269	391	761	272	26,1	0.707	28.840
Rubik Cu Plant, stream sediment 1 km below plant	299	359	239	314	11,1	0.362	10.600
Rubik Cu Plant, stream sediment 2 km below plant	310	736	275	145	24,1	0.409	19.050
Rubik Cu Plant, stream sediment 5 km below plant	264	394	200	198	10,2	0.256	9.611
Spaç Cu mine, stream sediment close to mine	77	25	589	229	25,1	0.322	49.670
Spaç Cu mine, stream sediment 2 km below mine	56	21	462	149	19,5	0.186	13.160
Spaç Cu mine, stream sediment 5 km below mine	63	26	490	156	9,9	0.193	14.600
Reps Cu factory, stream sediment 100 m below factory	242	111	262	178	10,2	0.200	15.100
Reps Cu factory, stream sediment 1 km below factory	91	61	420	275	16,8	0.289	23.810
Reps Cu factory, stream sediment 2 km below factory	103	101	248	195	11,6	0.199	17.720
Reps Cu factory, stream sediment 5 km below factory	110	119	289	322	13,8	0.312	16.740
Kurbnesh Cu factory, stream sediment closed to factory	354	50	1167	118	14,0	0.131	408.700
Kurbnesh Cu factory, stream sediment 100 m below factory	340	52	1130	113	13,9	0.120	301.200
Kurbnesh Cu factory, stream sediment 1 km below factory	376	190	1068	195	14,2	0.341	348.200
Kurbnesh Cu factory, stream sediment 2 km below factory	320	240	652	152	15,1	0.229	150.800
Mean	214.4	189.4	568.6	226.8	16.2	0.32	90.69
Median	253.3	114.9	476	195	14.1	0.27	21.16
Std. Deviation	116.5	194.9	335.6	123.1	5.6	0.19	135.7
Minimum	56	20.90	200	113	9.9	0.12	9.61
Maximum	375.8	736.0	1167	618	26.1	0.83	408.7

*Confidence Level (95%); **Fe (g kg^{-1} dry weight)

The river sediment samples show significant dilution of heavy metals downstream from Rubiku (except Ni and Cr) and Spaçi sites, and significant enrichment of heavy metals downstream from the Repsi (except Cr) and Kurbneshi (except Cr, Cu, and As) sites. The higher Ni concentration in sediment at RuSP4 (Fani River) could be related to the effluents from the Cu-electrolysis Plant, where Au, Se and Te are sorted out from Cu, at this sampling site. The elevated concentration of Ni and Cr in sediment, at this sampling site, could also be related to the geologic background (ultrabasic rocks), where the plant is placed.

However, concentrations of Cu, Zn at all the studied sites, Cr at Rubiku and Kurbneshi sites and at three sampling points of Repsi site ($ReSP_2$, $ReSP_4$, $ReSP_5$), Ni at Rubiku, Spaci and Kurbneshi sites, Cd at one sampling point of Rubiku site ($RuSP_1$), As in one sampling point of Spaci site ($SpSP_2$) and at Kurbneshi site, exceed the background concentrations for standard soil or sediment (Dutch Standards, Crommentuijn et al., 2000) Background concentrations represent the contents found in nature reserves plus atmospheric depositions (Alloway, 1995). While the concentrations of Cu (at all the samplings points), Ni (at four to five sampling points in Rubiku and at one to four sampling points in Kurbneshi) and As (at all the samplings points in Kurneshi and at one to three sampling points in Spaçi) exceed the intervention values. The results suggest that the geochemical baselines distant for these metals are >5 km from the studied sites. According to Gray (2003), the distance generally is >8 km.

The concentrations of Ni (Rubiku site), Ni, Pb, Zn and Cd (Spaçi site), Cr, Ni, Cu, Zn, Cd and Pb (Repsi site), and Ni and Cu (Kubneshi site) in sediment samples were higher than those in ore and calcine material from the corresponding site. This could be attributed to other polluting sources below or up the studied sites (the rivers flow through the residences).

The concentrations of Cr, Ni, Cu, Zn and As in sediment samples collected in this study are generally higher than those reported in the literature (Table 3) (Crommentuijn et al., 2000; Ramos et al., 1999; Bryan & Hummerstone, 1977), including background and maximum values (Geochemical Atlas of Europe, De Vos & Tarvainen, 2006).

Table 3. Comparison of heavy metal concentrations in sediment samples collected in this study (mg/kg of dry weight) with those published in literature.

Source	*Cr*	*Ni*	*Cu*	*Zn*	*Pb*	*Cd*	*As*
This study	56-375.8	20.9-736	200-1167	113-618	9.9-26.1	0.12-0.83	9.61-408.7
Crommentuijn et al., 2000	100	35	36	140	85	0.8	29
Ramos et al., 1999	-	-	2.23-37.4	20.6-198.5	2.82-69.7	0.23-1.25	-
Bryan & Hummerstone, 1977	59	57	65	329	155	1.3	-
De Vos & Tarvainen, 2006	48[a]/1750[b]	46[a]/1200[b]	34[a]/998[b]	141[a]/11400[b]	39[a]/4880[b]	0.821[a]/43.1[b]	19[a]/231[b]

[a]90^{th} percentile; [b]Maximum

Table 4. Correlation coefficient (*r*) among heavy metals and between those and sediment properties[a]

	Cr	*Ni*	*Cu*	*Zn*	*Pb*	*Cd*	*As*
1. Rubik Copper Plant							
Zn	-0,907*						
Cd			0,986**				
As					0,940*		
pH			-0,988**			-0,984*	
0,930*	264	394	200	198	10,2	0.256	9.611
2. Spaç Cu-mine							
Cd				0,999*			
As				0,999*		1**	
Organic-C			1**				
3. Reps Cu-enrichment Factory							
Cd							
As		-0,954*		0,986*			
$CaCO_3$				0,961*			
4. Kurbnesh Cu-enrichment Factory							
Pb			-0,989*				
Cd				1 **			
pH		0.986*					
CaCO3			-0,972*			0,983*	
Organic-C							

r (correlation coefficients) are significant at $p < 0.05$ (*) or $p < 0.01$ (**); [a] No significant correlation coefficients are not shown here

According to concentrations of heavy metals in sediments, the studied rivers can be classified as slightly too markedly polluted by Ni, markedly to severe polluted by Cu, slightly to moderately polluted by Zn and Cd, and moderately to very severe polluted by As (Bratli, 2000).

3.3 Correlation analysis

Results of correlation analysis between heavy metal concentrations and sediment properties and among heavy metals are shown in Table 4. In many cases the correlation coefficients, although high, are not significant, because the data were few. Huong et al., (2007) reported similar results.

The correlation coefficients indicate that the Cu, Cd and As contents in sediments of Fani River and the Ni content in sediments of Uraka River are controlled by the pH. The Cu content in sediments of Sefa Stream is controlled by the organic carbon, the Zn content in sediments of Fani Vogel River, the Pb and Cu contents in sediments of Uraka River are controlled by the carbonates.

The lack of a relationship in sediment between metal contents and organic-C and carbonate contents could be explained due to the lower content of organic matter and carbonate in sediment (Korfali & Davies, 2004). In a number of cases, correlations among the heavy metal concentrations in sediments are significant, suggesting that the metals have a common source(s) (Ritter & Rinefierd 1983).

3.4 Total heavy metal concentrations in ore and calcine samples

Metal concentrations in ore and calcine samples varied greatly among the studied samples (Table 5). The range of values is as follows: Cu 250-126000 mg/kg, Zn 24-37502 mg/kg, Cd 0.01-5.84 mg/kg, As 28-1448mg/kg, Cr 40-519.4mg/kg, Ni 8.8-104.7mg/kg and Pb 4.5-103.1 mg/kg. The high standard deviation of most metals, except Cr, suggest that metal concentrations vary significantly in ore and calcine piles at individual sites.

3.5 Water leaching of heavy metals

Although the total concentrations of some metals in ore and calcine samples were highly elevated, the potential of these wastes to release heavy metals is more important (Gray, 2003). According to Luís et al., 2009 (quoted by Marin et al., 2010), the weathering of sulphide-rich mining waste causes acid mine drainage, while the effluents are characterized by low pH and contain significant quantities of sulphates, As, and heavy metals. Based on information obtained from the mining engineers, the Kurbneshi is a quartz-sulphide source, and therefore there is little pyrite associated with ores. While the Rubiku, Spaçi and Repsi sources are rich in pyrite. As a result, the potential for acid-water generation is variable. That is reflected to highly variable amounts of heavy metals found in the leachates.

The chemical properties and concentrations of metals in leachates are shown in Table 6. The Cd is from 0 to 0.31 mg/kg; the As is from 0 to 0.06 mg/kg; the Pb is from 0 to 0.04 mg/kg; the Ni is from 0 to 53 mg/kg; the Cu is from 1.0 to 16800 mg/kg; the Zn is from 0.4 to 81 mg/kg; pH is from 2.82 to 7.07, and conductivity is from 7.9 to 6090 µS/cm. The high standard deviation of metals Fe, Cd, Pb, Ni, Cu, and Zn indicate that the concentrations of these metals vary significantly in ore and calcine piles at individual sites. The highest metal concentrations (Cu 16800 mg/kg, Zn 81 mg/kg, Ni 53 mg/kg and Cd 0.313 mg/kg) were found in leachate obtained from one ore sample collected from the Rubiku site.

Leachates obtained from other calcine and ore samples contained relatively lower heavy metals, except Cu (113 mg/kg) in ore sample from the Spaçi site. The concentrations of Pb and Cr in leachates were below the detection limits.

There is no significant correlation between leachate Zn. Cd and As concentrations and Zn. Cd and As contents in the corresponding ores and calcines leached. While the leaching of these metals from ore could be due to the presence of soluble metal salts (Gray, 2003). On the other hand, there is a significant correlation for Cu (r=0.991. $p<0.01$), indicating a high potential of ore to release copper.

Leachate with the highest conductivity contains highest Cu. Zn and Cd concentrations. The correlations between these metals concentrations and conductivity were significant at $p<0.05$ (r=0.869. r=0.869 and r=0.881. respectively). However, the highest metal concentrations do not correlate significantly with pH (r=-0.24. r=-0.24 and r=-0.23. respectively), suggesting that the release of metals is not controlled by the capacity of ores and calcines to generate acid.

4. CONCLUSIONS

The results indicate that the contamination with heavy metals, derived from copper industries, is extended along Fani and Mati rivers. The concentrations of the analyzed heavy metals, in sediment samples, varied of the sampling sites. The observed enrichment of Cr, Ni, Cu, Zn, As and Cd downstream from the studied industrial sites could be related to effluents from other polluting sources like Cu-electrolysis plant in Rubik and residences in the study area. However, there is a downstream transference of the analyzed metals from the studied sites.

Table 5 Concentrations of heavy metals in ore and calcine samples (mg/kg of dry weight) collected in this study*

Location/description	*Cr*	*Ni*	*Cu*	*Zn*	*Pb*	*Cd*	*As*
Rubik Cu Plant, ore sample inside plant	135	97	126000	265	8,8	1.161	151.400
Rubik Cu Plant, calcine sample inside plant	407	9	3588	37502	103.1	1.258	28.160
Spaç Cu mine, ore sample from dumpsite	75	14	3896	43	< 5	0.012	57.190
Reps Cu factory, ore sample from dumpsite	40	10	250	65	4.5	0.013	56.510
Kurbnesh Cu factory, ore sample inside factory	286	105	17812	2330	28.9	5.838	521.400
Kurbnesh Cu Factory, ore sample outside the factory	335	15	2226	65	17.9	0.143	507.100
Kurbnesh Cu factory, ore sample from dumpsite	519	26	1228	24	5.2	0.012	1448.00
Mean	256.6	39.2	22142.9	5756.3	24.8	1.20	395.7
Median	285.6	14.7	3588	65	8.8	0.14	151.4
Std. Deviation	179.5	42.5	46180.3	14023.6	35.7	2.12	509.9
Minimum	40	8.8	250	24	4.5	0.01	28.2
Maximum	519.4	104.7	126000	37502	103.1	5.84	1448

*Confidence Level (95.0%)

Table 6 Chemical properties and heavy metals concentrations (mg/kg of dry weight) in leachates of ores and calcines*

Location/description	*Cr*	*As*	*Pb*	*Ni*	*Cu*	*Zn*	*pH*	*Conductivity*
Rubik, leachate of ore	0.313	0.054	0.028	53	16800	8	3.23	6090
Rubik, leachate of burned ore	0.001	N.D.	N.D.	N.D.	11	1.1	5.96	7.9
Rubik, leachate of ore	0.003	N.D.	N.D.	N.D.	113	1.1	3.2	934
Spaç, leachate of ore	0.003	0.046	N.D.	N.D.	11	1.9	2.82	1970
Reps, leachate of ore	0.011	0.025	N.D.	N.D.	1	0.7	7.07	2417
Kurbnesh, leachate of ore	0.013	0.021	0.037	N.D.	29	1.5	3.21	2530
Kurbnesh, leachate of burned ore	0.002	0.055	N.D.	N.D.	26	0.4	3.41	2447
Mean	0.05	0.03	0.01	7.57	2427.3	12.5	4.13	2342.3
Median	0.00	0.03	0.00	0.00	26.00	1.10	3.23	2417.0
Std. Deviation	0.12	0.02	0.02	20.0	6337.9	30.2	1.67	1900.4
Minimum	0.00	0.00	0.00	0.00	1.00	0.40	2.82	7.90
Maximum	0.31	0.06	0.04	53.0	16800	81.0	7.07	6090

*Confidence Level (95.0%); N.D. = not detected

In several sampling sites, the concentrations of Cr, Ni, Zn and Cd in sediment samples were above the background values, while the concentrations of Cu and As were above the maximum values (Geochemical Atlas of Europe). The studied rivers can be classified as slightly to markedly polluted by Ni, markedly to severe polluted by Cu, slightly to moderately polluted by Zn and Cd, and moderately to very severe polluted by As.

Samples of ore and calcine contain high concentrations of Cu, Zn, As, Cr, Ni and Cd and a high potential for pollution of environment with these elements. The leachates from ores and calcines generated variable, but significant in case of an ore sample from the Rubiku site, heavy metals (16800 mg/kg Cu, 81 mg/kg Zn, 53 mg/kg Ni and 0,313 mg/kg Cd) during the water-leaching study. The concentrations of these metals in sediment samples are also high.

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