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MINERALOGICAL AND GEOCHEMICAL STUDY OF THE KIRKI MINING WASTES, EVROS REGION, GREECE – DETERMINATION OF THE ENVIRONMENTAL IMPACT BY TOXIC AND HEAVY METALS

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Abstract

Mining activity at the Kirki ore deposit has occurred over short periods, from 1974 to1980 and 1990 to 1997. The mining wastes at the cracked tailing ponds and at other on-site locations of the plant, together with the remains of the mining concentrates, the piles of the unprocessed ore and the large number of destroyed and weathered barrels of chemical reagents, including sodium cyanide, are a great risk to public health. All these wastes are exposed to rain-water and constitute a permanent source of toxic metals and other materials, which are transported by the adjacent small river of Erini, contaminating the hydrologic system of the whole area including the city of Alexandroupolis. For example, the concentrations of toxic metals such as Pb, Cu, Zn, As and Cd in the clay fraction of the river sediments is 2100, 300, 50, 100 and 660 times, respectively, above the natural background concentrations.

Key words: *Acid drainage, soil contamination, metal-bearing wastes.*

Περίληψη

Τα μεταλλεία της Κίρκης λειτούργησαν σε μικρά χρονικά διαστήματα κατά τα έτη 1974-1980 και 1990-1997. Τα μεταλλευτικά απόβλητα στις κατεστραμμένες λεκάνες εναπόθεσης καθώς και σε άλλους χώρους της περιοχής του εργοστασίου εμπλουτισμού, μαζί με τα υπολείμματα των μεταλλευτικών συμπυκνωμάτων, τους σωρούς ακατέργαστου μεταλλεύματος και πλήθος κατεστραμμένων και αποσαθρωμένων βαρελιών χημικών αντιδραστηρίων, μεταξύ άλλων και κυανιούχου νατρίου, απειλούν άμεσα τη δημόσια υγεία. Όλα αυτά τα απόβλητα είναι εκτεθειμένα στο νερά της βροχής και αποτελούν μία διαρκή πηγή τοξικών μετάλλων και άλλων υλικών, τα οποία μεταφέρονται στο γειτονικό ποταμό Ειρήνης, με αποτέλεσμα την μόλυνση του υδρολογικού συστήματος όλης της περιοχής, συμπεριλαμβανομένης και της πόλης της Αλεξανδρούπολης. Για παράδειγμα, οι περιεκτικότητες του αργιλικού κλάσματος των ιζημάτων του ποταμού σε τοξικά μέταλλα όπως Pb, Cu, Zn, As και Cd είναι 2100, 300, 50, 100 και 660 φορές μεγαλύτερες από τις καθορισθέντες οριακές τιμές, αντίστοιχα.

Λέξεις κλειδιά: *όξινη απορροή, μόλυνση εδάφους, μεταλλούχα απόβλητα.*

1. Introduction

Mining has been a very important economic activity in Northern Greece since antiquity, due to the significant metal-rich ore deposits which occur within the different geological environments of the area. The result of this activity is significant environmental pollution, since mining is one of the major sources of toxic and heavy metal contamination (Kelepertsis and Bibou 1991, Astaras *et al.* 1997, Darlagiannis *et al.* 2002, Kitsopoulos and Pavlidou 2004, Karatasou *et al.* 2005, Damigos and Kaliampakos 2006, among others).

The case study of the Kirki ore-district pollution has been previously published by Watzl (1998), Finitsi *et al.* (2002), Arikas *et al.* (2004), Skarpelis and Triantafyllidis (2004), and Asfahani *et al.* (2005). The mixed-sulfides mine of Saint Philippos in Kirki, located 6 km to the northeast, and particularly the flotation plant, located 3 km east of Kirki (Fig. 1), have caused great environmental damage during the relatively short operation periods of 1974-80 and 1990-97. The mining wastes at the cracked tailing ponds (Fig. 1) and at other locations of the plant, the remains of the mining concentrates, the piles of the unprocessed ore and the large number of destroyed and weathered barrels with chemical reagents, including sodium cyanide, are a great risk to public health. All these wastes are exposed to rain-water and constitute a permanent source of toxic metals and other materials, which are transported via the adjacent small river of Erini which flows to the south, and which discharges 23 km downgradient into the Thracean Sea, east of the city of Alexandroupolis (Fig.1).

Poor management during the past mining and mineral processing has led to a significant environmental loading of the region with toxic leachate and toxic metals, such as Pb, Zn, Cu, As, Cd and others. The oxidation and the erosion of the sulfides within the tailing ponds and from the mineral concentrates has lead to the formation of new sulfate minerals, increasing the acid drainage and the emission of toxic metals into the hydrologic system (Arikas *et al.* 2004).

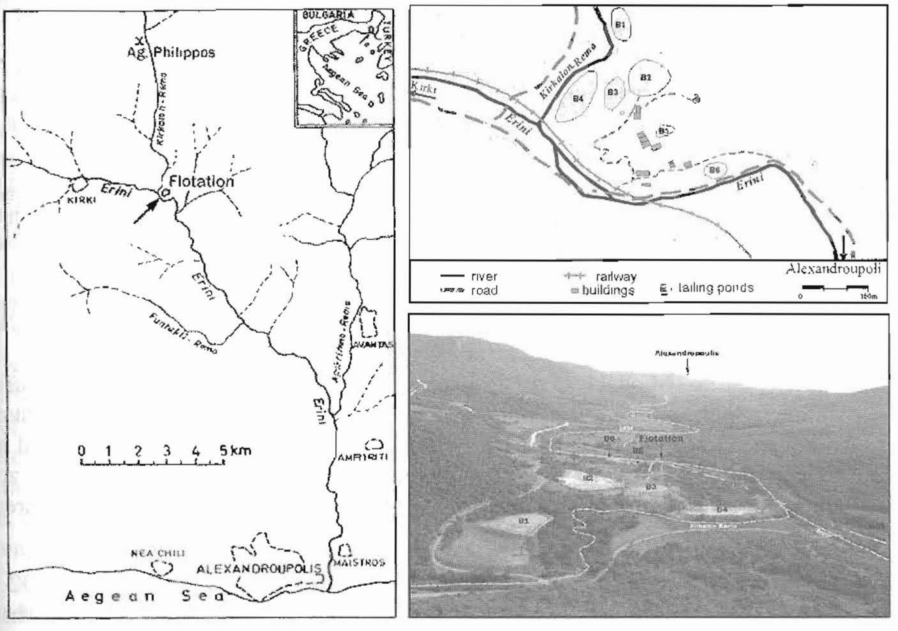

Figure 1 - Sketch maps and a figure of the studied area. Left figure: Sketch of the drainage pattern of the Erini River and the area around Kirki, the Saint Philippos mine and Alexandroupolis. At the right side (top) the detail of the flotation plant and the tailing ponds are shown. Right side (bottom): Panoramic view of the flotation plant. B1-B6: tailing ponds. The dashed lines show the rivers of Kirkalon and Erini. (Picture taken from the Tigris Hill from the northwest)

This study presents new mineralogical and geochemical data of three exceptionally polluted districts near Kirki in the region of Evros, which are 1) the tailing ponds and ore mineral concentrates, 2) the soils around the plant area and 3) the sediments of the Erini River, in order to determine the concentrations of the various heavy and toxic metals and the related minerals which carry such metals.

2. Analytical Techniques

Sampling was carried out during the years 1998 to 2005. The mineralogical and geochemical studies include: 1) the tailing ponds and ore mineral concentrates, 2) the area around the plant and 3) the sediments of the Erini River. Special care was assigned in the sampling of the six tailing ponds, where 80 cm deep sections were dug and a total of 29 samples were obtained (3 to 9 samples per section). In pond B4 the section was 110 cm deep, due to the erosion by rain water. Additional sampling was carried at the surface (2 cm deep) of the ponds where whitish fine-grained secondary minerals have been formed.

Clay minerals in the selected samples were identified by X-ray diffraction (XRD) analysis of whole-rock samples and clay fractions (<65 μm) at the University of Hamburg. The geochemical study is based on a total of 180 chemical analyses for major and trace elements, measured with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Total Reflection X-Ray Fluorescence (TXRF) and Atomic Absorption Spectrometry (AAS) at the University of Hamburg. The results focus on the following heavy metals: Fe, Mn, Pb, Zn, Cu, As and Cd, which are present in the mined and processed ore.

3. Geological setting

The geology of the studied area is dominated by Oligocene synorogenic subvolcanic stocks and dikes of calc-alkaline to high-K calc-/alkaline affinity. The magmatism resulted from the underthrusting of the African plate beneath the southern margin of the Eurasian plate and is attributed to slab break-off and/or slab delamination mechanisms (De Boorder *et al.* 1998, Christofides *et al.* 1998). A basal-clastic formation of Middle to Upper Eocene age including tuffaceous material (Papadopoulos 1982) discordantly covers the high to ultra-high grade metamorphic basement of the Rhodope massif (Mposkos and Kostopoulos 2001). A volcanic sequence consisting of lava domes, flows and pyroclastics of andesitic to dacitic composition was intruded at about 32 Ma (Del Moro *et al.* 1988) by I-type subvolcanic dacite-andesitic and monzodioritic bodies. All the above lithologies are cut by rhyolitic dikes, which were intruded mainly along NNW-SSE trending faults.

The hydrothermal Pb-Zn deposit of Agios Philippos, north of Kirki (Fig. 1), NE-Greece, occurs as fracture fillings and breccia-hosted sulfides and sulfosalts in a tectonic zone bounded by two pre-mineral subvertical faults (Michael *et al.* 1989, Dimou 1994, Skarpelis 1999, Voudouris *et al.* 2005). Rhyolites, which predate the mineralization, intruded the volcano-sedimentary host lithology. An advanced argillic alteration with alunite and minor pyrophyllite followed an early pervasive grey silicification of the rocks. Propylitic and sericitic hydrothermal alteration zones are developed peripheral to the ore zone. A part of the deposit comprises hydrothermal breccias of previously silicified sedimentary rock and rhyolite.

Exploration for Pb and Ag ores in the area of Kirki began late in the 19th century. In 1932 English mining companies invested in exploration projects, started construction of mine shafts and managed to exploit 20,000 tn of ore. With the onset of the World War II, the German company "Thrazische Bergwerke" continued exploration in the Agios Philippos area. Small scale exploitation commenced and a part of a flotation plant with an 80 tn/day capacity was installed. Exploration for base metals and Ag in the following years was carried out by several state owned Greek agents. In 1973 the lease was sublet to "Evros Mining Co" between 1974 and 1980 (underground since 1977), which exploited and processed roughly 160,000 tn of ore at 4 to 10 % combined Pb and Zn. Pb concentrates at 60-70 % Pb, 3-7 % Cu and 500 gr/tn Ag, and Zn concentrates at 48-54 % Zn and 0.4-0.5 % Cd were produced. With several long interruptions, open pit mining and processing of the ore continued from 1990 up to 1997 and possibly 50,000-70,000 tn of ore were extracted.

On the basis of mineralogical studies (Moëlo *et al.* 1985, Vavelidis *et al.* 1989, Michailidis *et al.* 1989, Dimou 1994, Skarpelis 1999, Voudouris *et al.* 2005) the following mineral composition has been determined: pyrite (FeS_2), sphalerite (ZnS), wurtzite (ZnS), galena (PbS), jordanite ($Pb_{14}As_6S_{23}$), Bi-jordanite ($Pb_{14}BiAs_5S_{23}$), kirkiite ($Pb_{10}Bi_3As_3S_{19}$), cosalite ($PbBi_2S_5$), tennantite ($Cu_{12}As_4S_{13}$), chalcopyrite ($CuFeS_2$), marcasite (FeS_2), bismuthinite (Bi_2S_3), kesterite (Cu_2ZnSnS_4), luzonite (Cu_3SbS_4), stibioluzonite (famatinite-Cu_3SbS_4), enargite-stibioenargite ($Cu_3(As,Sb)S_4$), seligmannite ($CuPbAsS_3$), bournonite ($CuPbSbS_3$), levyclaudite ($Pb_8Sn_7Cu_3(Bi,Sb)_3S_{28}$), arsenopyrite ($FeAsS$), stannite ($Cu_2FeSnS_4$), bornite ($Cu_5FeS_4$), and covellite ($CuS$). Quartz, kaolinite/dickite, alunite and barite are the gangue minerals closely associated with the ore. Massive wurtzite aggregates fill open spaces either of the ore or the silicified rocks, usually filling the inner wall of cavities. It is evident that wurtzite was the last formed sulfide mineral. Electron microprobe analysis from Driesner and Pintea (1994) revealed interesting trace element contents in wurtzite from Kirki: the Fe- and Mn-content is below detection limit, Cd reaches up to 2.6 wt%, In up to 3.5 wt%, Ga 1.6 wt% and Ge <0.3 wt%, while Hg, Sn and Ag usually are below detection limit.

Euhedral to subhedral barite crystals accompany sulfides and sulfosalts throughout the ore zone. Calcite, dolomite and rarely rhodochrosite are found in veins and veinlets crosscutting the ore, especially in the deeper parts of the mineralized zone, indicating they were the late formed hydrothermal minerals.

4. Results

4.1. The tailing ponds and mineral concentrates

The mineralogical study of the six tailing ponds (Figs 1, 2) which occur close to the flotation plant, revealed the presence of the typical hydrothermal-alteration minerals such as quartz, kaolinite, pyrophyllite, gypsum and sericite, as well as the most common ore minerals of the deposit, pyrite, galena and sphalerite/wurtzite.

In addition, the whitish fine grained secondary minerals (Fig. 2) formed at the sides of the tailing ponds due to the erosion of the mining wastes and the mineral concentrates, are considered to be of great importance for the environmental loading of the area. These minerals consist mainly of two various secondary sulfate salts: a halotrichite-dietrichite group-$(Fe,Mn,Zn,...)Al_2(SO_4)4.22H_2O$ and a rozenite-boyleite group-$(Zn,Fe,Mn,....)(SO_4).4H_2O$. Both mineral groups area characterized by absorbing high concentrations of Mn, Fe, Pb, Cu and mainly S, Zn and Cd, and as they are water soluble, they play a major role in the release of these metals into the environment and into the hydrologic system. Surface samples of pure whitish fine grained secondary minerals, mainly halotrichite and rozenite, contain up to 327,070 ppm S, 189,360 ppm Zn and 2,250 ppm Cd. In addition, due to their high sulfur coutent, they increase the acid drainage of the whole area. Whole-rock chemical analyses (Table 1) of the surface samples of the tailing ponds containing these salt sulfates, showed extremely high concentrations in heavy metals such as Pb up to 12,620 (51,450) ppm, Cu up to 1,310 (5,750) ppm, Zn up to 57,830 ppm, As up to 490 (1,185) ppm and Cd up to 1,070 ppm.

The chemical analyses of the tailing ponds (Table 1) revealed up to 14,600 ppm Pb, 22,740 ppm Zn, 3,900 ppm Cu, 944 ppm As and 193 ppm Cd. These results confirm the suggestion that the enrichment processing of the ore mineralization was insufficient which led to the loss of significant quantities of ore, which has been transported and has accumulated in the tailing ponds.

Great piles of mineral concentrates remained inside and around the plant. Chemical analyses from the 8 concentrate piles are listed in table 2. The main ore minerals identified here are pyrite, galena and sphalerite/wurtzite. Some ore has been oxidized and secondary minerals such as goethite and anglesite also occur. Hydrous salt sulfates are also found and the most widespread is rozenite-boyleite. The chemical analyses of the concentrates (Table 2) revealed up to 37,680 ppm Pb, 188,740 ppm Zn, 17,650 ppm Cu, 5,240 ppm As and 1,350 ppm Cd.. Samples rich in sulfate salts from the eroded surface of the concentrate piles contain up to 254,850 ppm Zn and 2,560 Cd. (Table 2).

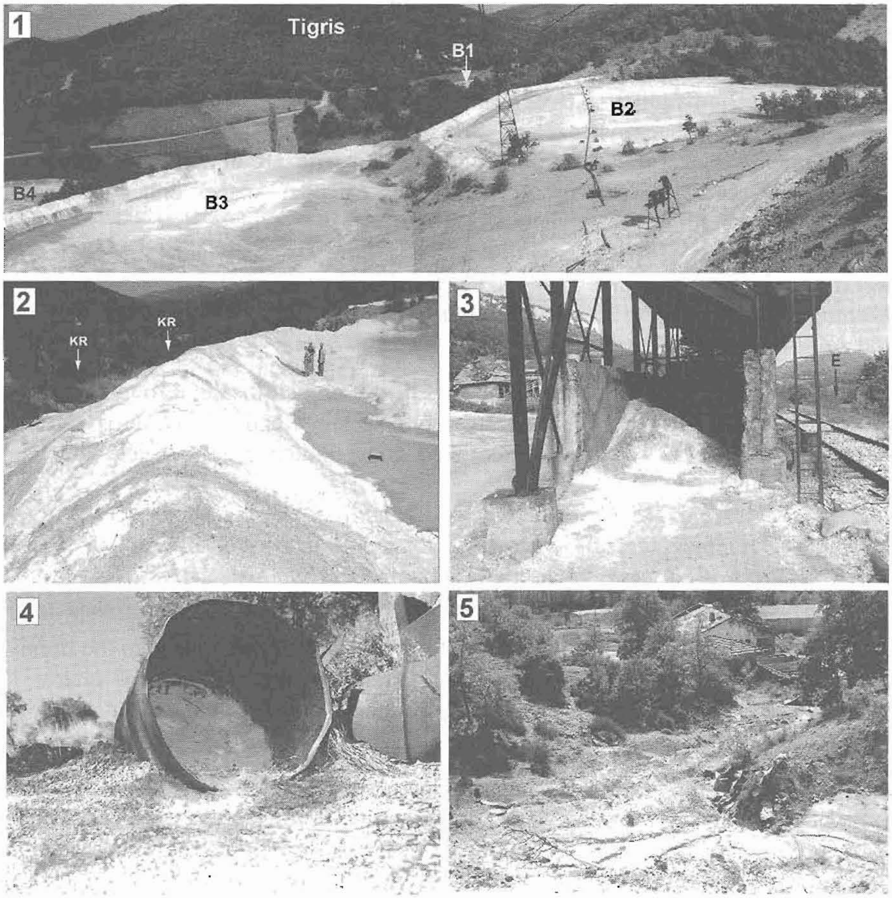

Figure 2 - Photographs from the area around the flotation plant in the Kirki area 1. The tailing ponds (B1-B4) at the northeastern site. Tigris hill is in the background, 2. The tailing pond B3 with an intense white snrface due to the formation of sulphate salts, part of which, evidently, are transported by the Kirkalon Stream (KR) and then by the Erini River, 3. Stocks of the ore-mineral concentrates at the flotation plant and the characteristic white areas, 4. An open destroyed barrel containing remains of an unknown chemical reagent, possibly cyanide solutions, 5. Free transportation of the white coloured sulphate salts and the tailing ponds along channels at the eastern part of the plant towards the Erini River (in the background of the picture)

From the correlation of the various heavy metals (Fig. 3) in the tailing ponds and in the ore-mineral concentrates, it is evident that the As content correlates with Pb and especially with Cu content, since As is found mainly in the copper bearing minerals. In addition, a positive correlation is evident between Cd and Zn because they are both found in sphalerite and wurtzite.

4.2. The area around the flotation plant

The area around the flotation plant is extremely contaminated because it is covered by scattered mining wastes and mineral concentrates, as well as by a large number of damaged barrels with various chemicals reagents, including sodium cyanide (Fig. 2). All these materials are exposed to the rain and the wind, and are dispersed throughout a wide area.

Table 1 – Concentrations (in ppm) of selected heavy metals from a total of 43 samples, in the sections of the six tailing ponds (B1-B6). T/1: lower content, T/2: higher content, T/3 average content. Su: higher content of the surface samples (depth of 0-2 cm)

Tailing Pond		B1	B2	B3	B4	B5	B6
Pb	T/1	3,147	2,570	4,024	4,341	8,192	8,414
	T/2	3,325	5,791	7,950	12,496	14,599	10,136
	T/3	3,230	4,321	5,845	6,572	10,382	9,173
	Su	4,486	3,777	8,477	9,464	12,623	51,452
Zn	T/1	7,786	3,495	8,861	802	10,342	10,434
	T/2	8,744	14,831	20,190	4,411	22,740	17,595
	T/3	8,299	9,783	13,483	2,469	14,972	14,071
	Su	7,007	42,959	57,833	23,826	6,777	53,390
Cu	T/1	346	192	174	121	2,346	483
	T/2	694	262	388	609	3,895	556
	T/3	467	195	267	252	2,940	509
	Su	1,153	252	514	874	1,313	5,750
As	T/1	196	72	99	104	620	199
	T/2	262	133	139	193	944	255
	T/3	222	106	124	139	733	223
	Su	461	145	171	235	488	1,185
Cd	T/1	90	28	77	5	71	80
	T/2	93	118	132	46	193	188
	T/3	91	81	106	22	123	124
	Su	60	236	1,070	531	61	267

In order to evaluate the impact of the various heavy metals in the sediments and soils, a series of standard, natural background values have been determined, after analysing uncontaminated sediments and soils of the studied area. Therefore, it would be possible to compare the chemical composition of the soils around the plant with the standard compositions and estimate the level of the contamination. These standard values are: 18 ppm for Pb, 72 ppm for Zn, 22 ppm for Cu, 15 ppm for As and 0.2 ppm for Cd.

The soils and the sediments in the vicinity of the flotation plant are also very highly contaminated (Table 3), although their chemical composition shows a large heavy metal fluctuation. Almost all the samples contain over 5,000 ppm Pb and Zn. In places, the concentrations of Pb, Zn, Cu, As and Cd reach up to 33,400 ppm, 40,000 ppm, 2,500 ppm, 1,700 ppm and 290 ppm, respectively. These values are respectively 1850, 555, 115, 110 and 1450 times higher than the standard background values.

4.3. The sediments of the Erini River

The heavily contaminated tailing ponds and mineral concentrates, as well as the piles of unprocessed run-of-mine (ROM) material and the chemical reagents, sodium cyanide among them, constitute a long-term source of toxic metals and harmful compounds in the area of the flotation plant, being dangerous to public health. All these mining wastes are exposed to rain water, and thus the mobile elements are transported into the hydrologic network, mainly via the nearby small Krikalon Stream and then via the Erini River (Figs 1, 2) which discharges to the Thracean Sea, east of Alexandroupolis.

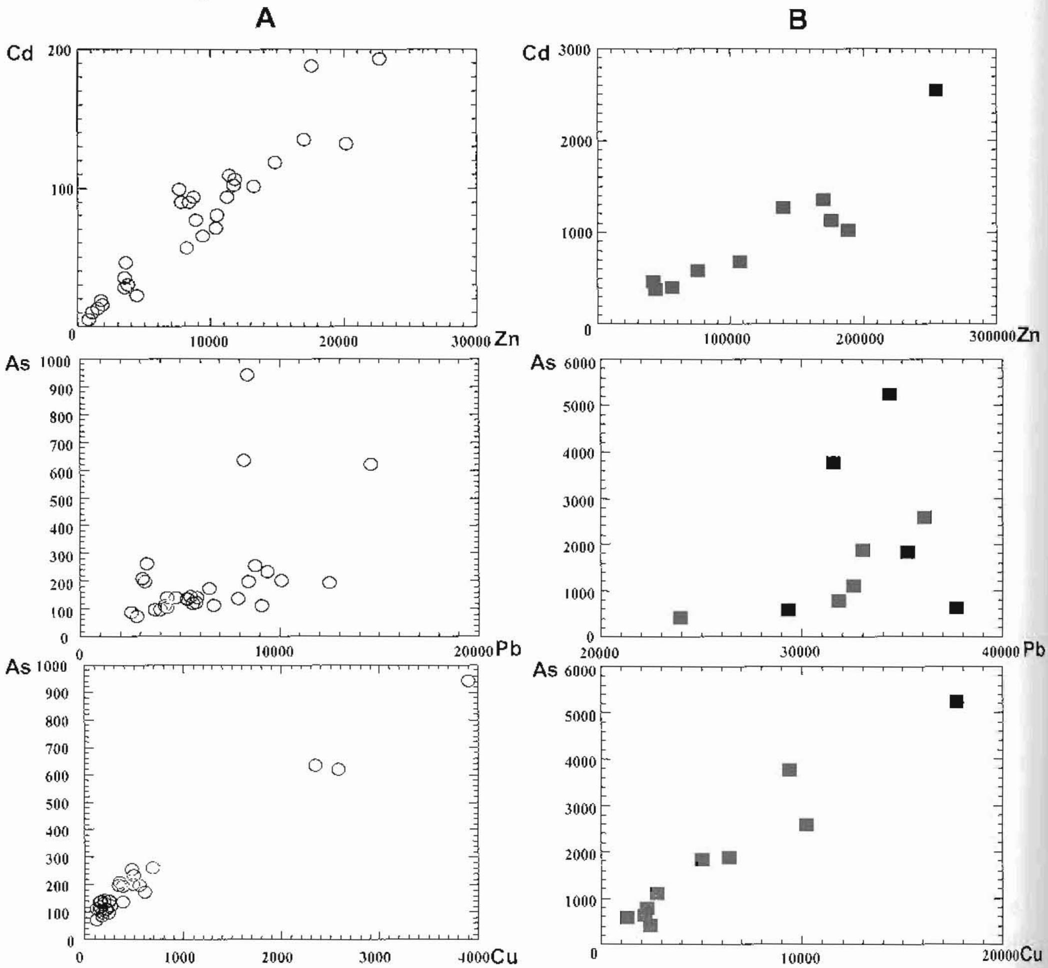

Figure 3 - Correlation of the heavy metals Pb, Zn, Cu, As and Cd, in the tailing ponds (A) and in the mineral concentrates (B)

The chemical analyses of the sediments along the Erini River have been presented by Arikas *et al.* (2004). The Pb concentrations reach 22,830 ppm, Zn 6,210 ppm, Cu 760 ppm, As 1,700 ppm and Cd 51 ppm. These concentrations are respectively 1270, 85, 35, 115 and 255 times higher than the background values of the sediments. In the clay fraction of these samples the following heavy metals: Pb (up to 37,800 ppm), Zn (up to 21,550 ppm), Cu (up to 1,030 ppm) and Cd (up to 133 ppm), are respectively 2100, 300, 47 and 665 times higher than the standard background values. These particularly high values, within the clay fraction of the sediments, are very important because of the fact that they are transported very easily in the river waters.

Table 2 - Chemical analyses (in ppm) of the scattered mining wastes and mineral concentrates. K1-K7: piles of concentrates in the plant, K8: piles of concentrates at the disposal site, 50 to 70 m from the plant, K3a and K8a: secondary minerals from the surface of the relative piles K3 and K8

Sample	Co	Mn	Fe	Pb	Zn	Cu	As	Cd	S
K1	268	616	51,970	31,818	75,193	2,282	783	579	94,594
K2	216	12,753	100,641	35,274	56,393	5,026	1,830	400	147,853
K3	201	11,009	83,492	32,542	43,606	2,787	1,106	378	114,901
K3a	267	21,882	77,580	33,006	139,814	6,376	1,880	1,267	176,528
K4	100	7,743	53,793	29,311	41,705	1,269	591	□65	84,628
K5	296	5,554	112,140	34,365	106,799	17,651	5,243	683	196,781
K6	372	7,685	123,741	36,081	188,745	10,220	2,581	1,020	254,233
K7	273	8,367	60,847	37,678	176,142	2,175	620	1,135	175,688
K8	299	619	67,396	31,572	169,748	9,397	3,773	1,353	156,562
K8a	187	1,197	20,824	23,951	254,855	2,460	415	2,553	140,766

Table 3 – Chemical analyses (in ppm) of samples from the soil and the surface sediments around the flotation plant. Samples of sections, 65 cm deep (F12*: 0-15 cm, F13*: 15-25 cm, F14*: 25-45 cm and F15*: 45-65 cm)

Sample	Pb	Zn	Cu	As	Cd
F1	1,778	2,499	140	66	19
F2	1,979	3,147	133	58	27
F3	4,530	8,145	211	347	47
F3a	3,186	3,399	349	176	45
F4	9,126	20,333	554	233	205
F5	16,549	18,994	603	264	178
F6	33,362	40,015	2,522	787	293
F7	128	214	33	13	1,7
F8	31,459	16,549	2,118	1,732	134
F9	11,132	6,666	647	297	31
F10	10,568	9,091	449	211	70
F11	37,380	78,165	3,100	1,259	703
F12*	5,321	6,188	304	112	52
F13*	6,598	1,406	116	82	10
F14*	16,515	1,888	522	317	10
F15*	360	625	79	87	7,3
F16	2,945	4,898	189	156	65
F30	6,977	1,435	376	285	10

In the diagrams of figure 4A it is shown that in both the loose sediments and the sediments of the 1st terrace of Erini River, the correlations of Zn-Cd, Pb-As and Cu-As are positive as in the tailing ponds and the soils around the flotation plant. In contrast to the others, a few samples of the 1st terrace show especially high concentrations of Pb and As.

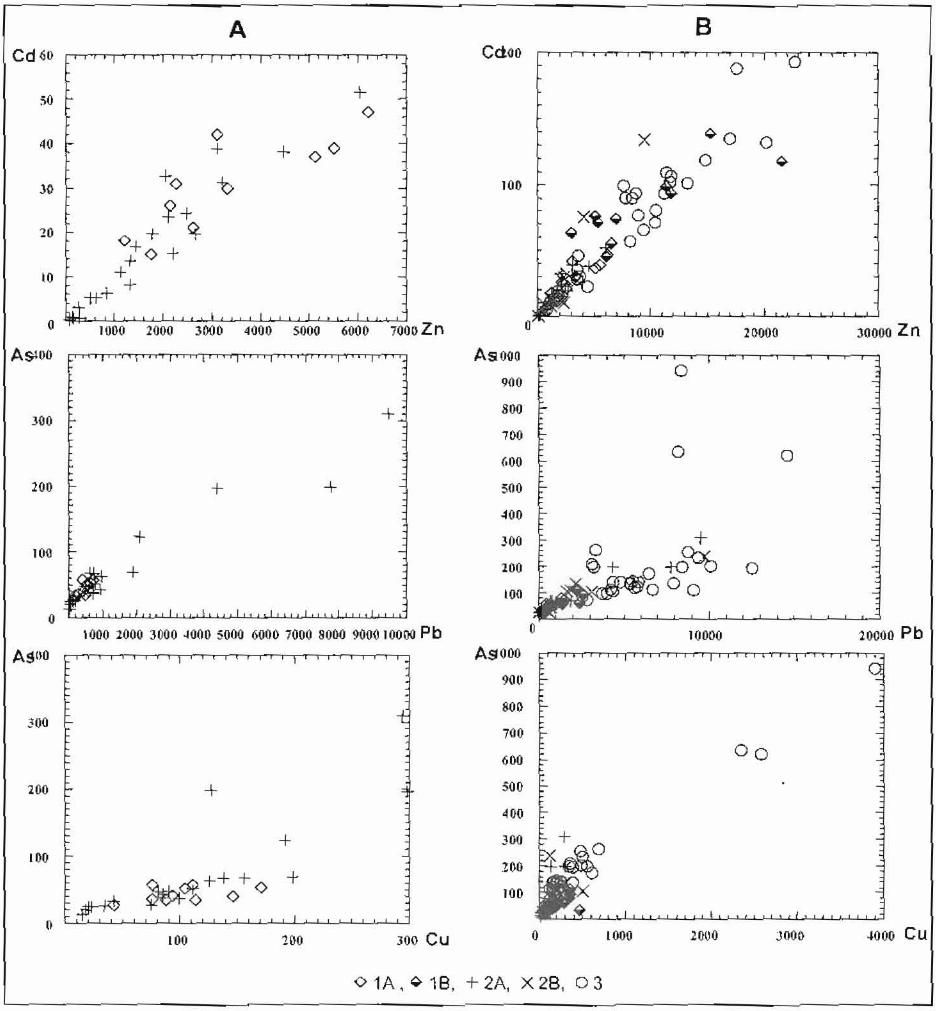

Figure 4 - Correlation of the heavy metals Pb, Zn, Cu, As and Cd, in the stream sediments (1A), in the sediments of the 1st terrace (2A) of the Erini River, their respective clay fractions (1B, 2B) and in the tailing ponds of the plant (3) for comparison

5. Conclusions

The present mineralogical-geochemical study demonstrates the extremely high risk to the environment and to public health, due to the heavy and toxic metal contamination of the area around the flotation plant and the Erini River near Kirki in the region of Evros. The tailing ponds, the soils and the sediments in the vicinity of the plant as well as the sediments of the river contain extremely high levels of Pb, Zn, Cu, As and Cd.

Field observations revealed that the "walls" of the six roughly-manufactured tailing ponds have been cracked, resulting in the discharge of the metal-bearing wastes and the sulfate salts in the stream of the adjacent Erini River. In addition, the mining area is saturated by scattered mining wastes and mineral concentrates, as well as by a large number of damaged barrels with various chemicals reagents, including sodium cyanide.

The most dangerous mineral species are the various sulfate salts which are the products of weathering of the mining wastes and which adsorb high quantities of Pb, Cu and especially S, Zn and Cd, and as they are easily dissolved in water, they constitute the best carrier of heavy metals into the hydrologic system. In addition, due to the high sulfur content, they increase the acid drainage of the area. Facing the dangerous contamination of the hydrologic system from these toxic metals, it is important to check the existing wells close to the Erini River, which are used for the supply of drinking water in various areas within the Municipality of Alexandroupolis. A complete proposal for an effective remediation of the Kirki mining-waste site is planned for the future.

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