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Heavy Metal Pollution Associated with an Abandoned Lead–Zinc Mine in the Kirki Region, NE Greece

**Christos Nikolaidis · Ilias Zafiriadis ·
Vasileios Mathioudakis · Theodore Constantinidis**

Abstract The "Agios Philippos" mine in the Kirki region (NE Greece) has been abandoned in 1998 after half a century of ore exploration without a reclamation or remediation plan. This article aims at elucidating the potential environmental risks associated with this site by quantifying pollution in tailing basins, stream waters, stream sediments and agricultural fields. Concentrations of heavy metals in the abandoned mine tailings reached 12,567 mg/kg for Pb, 22,292 mg/kg for Zn, 174 mg/kg for Cd and 241 mg/kg for As. The geoaccumulation index and enrichment factor for these metals were indicative of extremely high contamination ($I_{geo} > 5$) and extremely high enrichment (EF > 40), respectively. Stream waters in the proximity of the mine had an acidic pH equal to 5.96 and a high sulfate content ($SO_4^{-2} = 545.5$ mg/L), whereas concentrations of Mn, Zn and Cd reached 2,399 μg/L, 7,681 μg/L and 11.2 μg/L. High I_{geo} and EF values for Cd, Zn and As in stream sediments indicates that surface water pollution has a historic background, which is typically associated with acid mine drainage. Agricultural fields in the proximity of the mine exhibited high I_{geo} and EF values, which were in decreasing order Cd > Pb > Zn > As. These findings urge for an immediate remediation action of the afflicted area.

The first metallurgical exploration of the "Agios Philippos" mine in the Kirki region (NE Greece) began late in the nineteenth century. A small-scale underground exploitation took place between 1932 and 1934 and resulted in the production of approximately 20,000 tons of ore. During World War II the German company "Thraziche Bergwerke" installed a floatation plant with an 80 ton/day capacity and in the following years the Greek State and privately-owned companies took over the operation. Between 1976 and 1997 some 200,000 tons of sulfide ore have been extracted and processed. Ever since, the mine has been abandoned without any reclamation and/or rehabilitation of the afflicted area.

Around the abandoned mine there are five tailings basins. No drainage ditches, containment impoundments or surface land cover has been used to control the leaching of wastes (Triantafyllidis et al. 2007; Loupasakis and Konstantopoulou 2010). The dispersal of mining waste has been facilitated by surface runoff during rainfall, wind action and draining effluent. As a result substantial pollution of surface water, sediments and agricultural soil has taken place. In order to determine the degree and extend of heavy metal contamination associated with this site, samples from mine tailings, agricultural soils, stream water and sediments have been collected and analyzed.

Materials and Methods

Six surface water samples were collected along the course of the river (Fig. 1). Each sample consisted of two

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Fig. 1 Location of the study area and map of the Agios Philippos mine
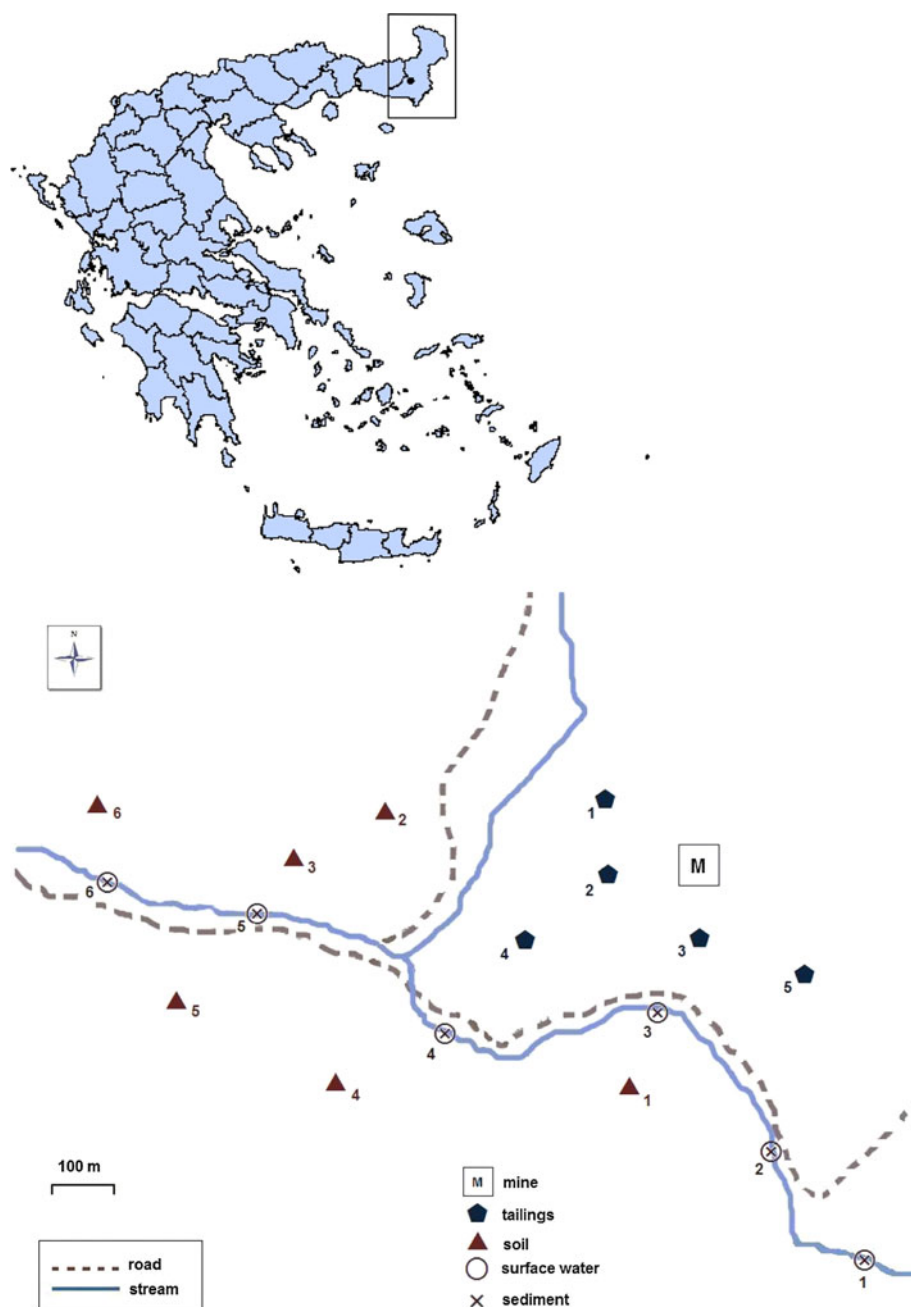
subsamples, one of which was acidified with HNO_3 to pH < 2 for metal analysis and the other was left unacidified for anion analysis. Electrical conductivity, pH and temperature were measured in the field. Five soil samples were collected from tailings basins scattered around the mine. Moreover, six soil samples were collected from agricultural fields in the proximity of the mine. Sediment samples were collected at exactly the same locations as surface water samples, in order to investigate the effect of acid mine drainage (Fig. 1). All solid samples consisted of about 200 g each and they were collected at a depth of 0–20 cm. Soil and sediment samples were dried at 70°C for

2 days and sieved through a 2 mm polyethylene sieve. They were then ground in an agate grinder until fine particles (<200 μm) and aliquots of 0.25 g were digested with 1 mL HNO_3 and 3 mL HCl (aqua regia). The solution was heated to 70°C and then deionized water was added to a final volume of 10 mL. Analytical determination of trace metal was carried out by Graphite Furnace Absorption Spectroscopy (Perkin Elmer AAnalyst 800). Arsenic was determined by Hydride Generation-Absorption Spectroscopy (Perkin Elmer AAnalyst 200) and anions were measured by Ion Chromatography (Dionex ICS-1000). For quality control, reagent blanks, duplicates and soil

international reference material (NIST 2709) were incorporated in the analysis to detect any contamination in the analytical materials and to assess precision and bias in the method. The analytical results showed no sign of contamination in the materials used. The recovery rates were in agreement with the certified concentrations (98% for Cu, 101% for Zn, 104% for Pb, 92% for As, 110% for Cd and 90% for Mn).

Results and Discussion

The mine is located in a mountainous area, shaped by narrow valleys and springs that form a complex hydrological network of approximately 20 km^2. Around the abandoned mine there are five tailings basins composed of largely conglomerate rocks with loose millet-seed sandstone texture, which exhibit weak water-tightness and are highly susceptible to erosion (Loupasakis and Konstantopoulou 2010). This is clearly evident in the perimeter, where ruptures and slidings of natural barriers are observed. The origin of the metalliferous ore in the Kirki region is sulphuric and pollymetalic. The mineralogy is classified as hydrothermal replacement type and mostly contains pyrite, sphalerite, galena, wurtzite and jordanite, where as secondary ore comprises of smaller amounts of tennantite, kasterite, cosalite and seligmanite (Triantafyllidis et al. 2007). This geochemical setting predisposes for acid mine drainage leading to heavy metal mobilization to the aquatic environment.

Six surface water samples were collected from the river traversing the mine area in the direction of flow from East to West. The results of the chemical analyses are presented in Table 1. A deterioration of quality characteristics, in terms of heavy metal content, ion concentration and pH was observed in samples 2–5. Sulfate content in these samples ranged between 256 and 545.5 mg/L exceeding EU drinking water guidelines. Accordingly, the pH of samples 2–5 appeared slightly acidic, ranging between 5.96 and 6.99. These findings are indicative of acid mine drainage originating from the mine's abandoned tailings basins (Olías et al. 2005; Chon and Hwang 2000). Samples 3 and 4 where particularly enriched in Mn, Zn and Cd. On the other hand, surface water concentrations of As, Pb, Ni, Cr, Cu and Fe were in compliance with the EU directive 98/83/EC.

Mine wastes from tailings basins and soil samples from agricultural fields were also collected from the study area to evaluate the distribution of metals within the surrounding environment (Table 2). Extremely high concentrations of Zn (22,292 mg/kg), Pb (12,567 mg/kg), Cd (174.1 mg/kg), Cu (1,201 mg/kg) and As (369.8 mg/kg) were recorded in tailings samples (T1–T5). The heavy metal content of agricultural soils was greater in samples A1–A3 that were closer to the mine portal (300–600 m), than in samples A4–A6, which were located further away (650–950 m). This indicates that the pollution of soils is directly related to the mining activities. In order to address the effect of acid mine drainage on the river system, six sediments samples (S1–S6) were collected and analyzed. The highest concentrations of Mn, Zn, Pb, Cd and As were recorded in samples S3 and S4. This suggests that the river has received a significant amount of contaminants in the course of time.

The effects of mining activities were further assessed using the geoaccumulation index (I_{geo}) and enrichment factor (EF) speciation. Igeo was introduced by Müller

Table 1 Chemical analyses of water samples

	1	2	3	4	5	6	EU drinking water standards*
pH	7.12	6.99	5.96	6.16	6,75	7.01	6.5–9.5
EC µS/cm	719	801	1,094	1,038	853	813	2,500
Ca mg/L	113.5	111	123.8	151.8	151.3	134.2	**
SO$_4$ mg/L	138	256	338.8	545.5	530.8	212	250
Fe µg/L	80	96	184	192	153	73	250
Cu µg/L	25	31	42	40	53	13	2,000
Mn µg/L	22.5	87.1	2,398.5	1,596.3	543.5	54	50
Zn µg/L	565.7	396	7,681	3,873.8	876.3	422.1	**
Cr µg/L	0.7	1.2	1.3	0.9	1.4	1.1	50
Ni µg/L	0.4	0.7	0.5	1.2	0.9	1.0	20
Pb µg/L	1.2	1.4	1.5	2.9	2.7	1.6	10
Cd µg/L	0.2	0.36	11.2	8.4	3.1	1.2	5
As µg/L	n.d.***	n.d.***	n.d.***	0.18	0.1	n.d.***	10

* Council Directive 98/83/EC, ** not specified, *** not detected

Table 2 Chemical analyses of mine tailings (T1–5), agricultural soils (A1–6) and stream sediments (S1–6)

mg/kg	Mn	Fe	Zn	Cu	Pb	Cd	As
T1	263.9	26,767	4,243	151.5	3,162	32.2	85.5
T2	231.5	33,103	2,504	604.5	12,567	15.4	241.1
T3	493.8	23,231	22,292	1,201	7,937	174.1	369.8
T4	396.4	20,198	14,064	572.3	4,449	75.4	151.9
T5	878.3	25,946	19,463	947.8	8,933	143.4	303.3
A1	450.5	36,551	345.1	28.3	80.4	3.2	8.9
A2	878.3	27,586	474	42.7	219	5.8	14.1
A3	1,212	22,517	256.3	37.7	195.4	2	11.4
A4	511.2	26,324	103.6	12.8	28.5	3.1	7.1
A5	607.4	22,455	56.9	17.4	36.3	1.2	4.7
A6	342.1	30,101	47.4	14.9	31	0.9	5.4
S1	453.2	22,000	101.2	26.7	39.7	0.7	8.35
S2	901	24,211	178.7	14.9	45.8	1.2	14.1
S3	5,180	27,543	3,986	58.6	302	34.7	24.6
S4	4,054	30,212	3,918	130.7	279.2	26.9	22.6
S5	2,469	21,546	2,750	26.7	110.4	16.4	18.3
S6	1,204	19,321	1,996	42.6	96.8	17.2	7.5

Table 4 Geoaccumulation index for mine tailings (T1–5), agricultural soils (A1–6) and stream sediments (S1–6)

	Cu	Mn	Zn	Pb	Cd	As
T1	2.0	−1.8	5.3	6.7	7.8	5.3
T2	4.0	−2.0	4.6	8.7	6.7	6.7
T3	5.0	−0.9	7.7	8.1	10.2	7.4
T4	3.9	−1.2	7.1	7.2	9.0	6.1
T5	4.7	0	7.5	8.2	9.9	7.1
A1	4.7	0	7.5	8.2	9.9	7.1
A2	−0.4	−1	1.7	1.4	4.4	2.0
A3	0.2	0.0	2.2	2.9	5.3	2.7
A4	0.0	0.4	1.3	2.7	3.8	2.3
A5	−1.6	−0.8	0	−0.1	4.4	1.7
A6	−1.1	−0.6	−0.9	0.3	3.0	1.1
S1	−1.3	−1.4	−1.2	0.1	2.6	1.3
S2	−0.5	−1.0	−0.1	0.4	2.3	1.9
S3	−1.3	0.0	0.8	0.6	3.0	2.7
S4	0.6	−0.8	5.2	3.3	7.9	3.5
S5	1.8	2.2	5.2	3.2	7.5	3.3
S6	−0.5	1.5	1.4	1.9	6.8	3.0

Table 3 Geoaccumulation index according to Müller (1969)

Class	Value	Soil or sediment quality
0	$I_{geo} \leq 0$	Uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated
4	$3 < I_{geo} < 4$	Heavily contaminated
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

(1969) and enables the assessment of contamination by comparing current and pre-industrial concentrations of heavy metals. This index is computed by the following equation $I_{geo} = \log_2 C_n/1.5B_n$, where C_n is the concentration of the element in the enriched samples and B_n is the background concentration of the element in the Earth's crust, according to Taylor and McLennan (1995). The factor 1.5 is used to address possible variations due to lithogenic effects (Stoffers et al. 1986). Müller (1969) has suggested 6 descriptive classes of geoaccumulation index (Table 3).

Heavy metal geoaccumulation in tailings samples shows extreme contamination with Cd, Pb, As and Zn (Table 4). Agricultural soils, however, exhibit various levels of geoaccumulation for different metals. Sample A1, which is located closer to the mine portal appears to be the most heavily contaminated. Geoaccumulation of Pb and Zn was very low in samples A5–A6, whereas As was moderately geoaccumulated and Cd heavily. Stream sediments S4 and

S5 were mostly affected. I_{geo} values for Cd and Zn, as well as Pb and As, were indicative of "extreme" and "heavy" contamination, respectively.

The enrichment factor was calculated using the formula $EF = (C_n/C_{ref})_{sample}/(B_n/B_{ref})$ originally introduced by Buat-Menard and Chesselet (1979), where C_n (sample) is the content of the examined element, C_{ref} (sample) is the content of the reference element, B_n is the background value of the examined element and B_{ref} (sample) is the background value of the reference element. In this study, Fe was used as the reference element at a crustal abundance value of 35,000 mg/kg (Taylor and McLennan 1995). Sutherland (2000) has proposed five contamination categories for EF: <2 = minimal enrichment, 2–5 = moderate enrichment, 5–20 = significant enrichment, 20–40 = very highly enriched, >40 = extremely highly enriched. The EF values for Zn, Pb, Cd and As in the tailings samples show extremely high enrichment (Table 5). Cadmium is the most polluting element in agricultural soils (A1–A5) with EF values ranging between 10.7 and 42.1. The elements Zn, Pb and As show significant enrichment only in samples A1–A3 and moderate enrichment in samples A4–A6. As regards stream sediments, cadmium appeared to be "extremely highly" enriched in all of the samples (S1–S6) with an EF value ranging between 271.8 and 2,676.5. Zinc was "extremely" enriched in samples S3, S4 and S6 and was "significantly" enriched in samples S3 and S4. Finally, arsenic showed "significant" enrichment in samples S2–S5, which is indicative of the acid mine drainage hypothesis discussed earlier.

Table 5 Enrichment factor in mine tailings (T1–5), agricultural soils (A1–6) and stream sediments (S1–6)

	Cu	Mn	Zn	Pb	Cd	As
T1	7.9	0.6	78.1	206.7	2,676.5	74.5
T2	25.6	0.4	37.3	664.4	1,333.2	169.9
T3	72.4	1.2	473.0	597.9	1,973.9	371.4
T4	39.7	1.1	343.2	385.5	31.3	175.5
T5	51.1	2.0	369.8	602.5	75.1	272.8
A1	1.1	0.7	4.7	3.8	31.7	5.7
A2	2.2	1.9	8.5	13.9	42.1	11.9
A3	2.3	3.1	5.6	15.2	19.1	11.8
A4	0.7	1.1	1.9	1.9	10.7	6.3
A5	1.1	1.6	1.2	2.8	11.4	4.9
A6	0.7	0.7	0.8	1.8	17.7	4.2
S1	1.7	1.2	2.3	3.2	449.9	8.9
S2	0.9	2.2	3.6	3.3	318.0	13.6
S3	3.0	1.1	71.3	19.2	271.8	20.8
S4	6.1	7.8	63.9	16.2	317.9	17.5
S5	1.7	6.7	6.3	9.0	2,676.5	19.8
S6	3.1	3.6	50.9	8.8	1,333.2	9.1

Hakanson (1980) proposed an overall indicator of contamination based on integrative data. This method is based on the calculation of contamination factor (C_f) according to the equation:

$$C_f = M_x/M_b$$

where M_x is the mean concentration of a pollutant from at least five samples in the contaminated site and M_b is the pre-industrial concentration of elements using the Earth's crust as a reference value (Loska et al. 2004). Hakanson (1980) has described four categories: $C_f < 1$ indicates low contamination, $1 \leq C_f < 3$ indicates moderate contamination, $3 \leq C_f < 6$ indicates considerable contamination, and $6 \leq C_f$ indicates very high degree of contamination. Figure 2 shows the contamination factors (C_f) for
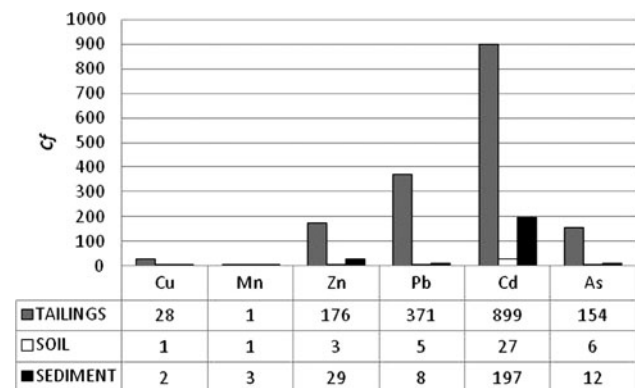
individual metals Cu, Mn, Zn, Pb, Cd and As in mine tailings, agricultural soils, and stream sediments. Again cadmium appeared to be the most polluting element. Very high contamination factors were recovered in the mine tailings that were in decreasing order Pb > Zn > As > Cu. Contamination of agricultural soils was moderate for Cu and Mn, considerable for Zn and Pb and very high for As and Cd. Stream sediments exhibited moderate contamination for Cu and Mn and very high contamination for all other elements, which were in decreasing order Cd > Zn > As > Pb.

Hakanson (1980) also proposed the use of a cumulative index defined as the degree of contamination (C_d), which is calculated by summing all individual contamination factors. Here we have used a modified version of this index, called modified degree of contamination (mC_d) introduced by Abrahim and Parker (2008). This is calculated by the following equation:

$$mC_d = \frac{\Sigma C_f}{n}$$

where n = number of analyzed samples and C_f = contamination factor. This generalized formula allows the incorporation of several metals without the restraint of an upper limit. The modified degree of contamination for tailings, agricultural soil and sediments in this study was 271.3, 7.0 and 41.8, respectively. This is indicative of a "high" degree of contamination for agricultural soils and an "ultra high" degree of contamination for abandoned tailings basins and riverine stream sediments (Abrahim and Parker 2008).

Overall these data show that the natural environment surrounding the "Agios Philippos" mine in the Kirki region (NE Greece) is severely contaminated by heavy metals (Cd, Pb, Zn, As and Cu). Precautionary actions should be considered in order to prevent the dispersion of pollution and avoid population exposures. Calculating these risks urges for an immediate remediation plan.

Fig. 2 Contamination factors (C_f) in mine tailings, agricultural soils and stream sediments from the Kirki mine (NE Greece)

	Cu	Mn	Zn	Pb	Cd	As
▪TAILINGS	28	1	176	371	899	154
▫SOIL	1	1	3	5	27	6
▪SEDIMENT	2	3	29	8	197	12

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