Environmental impacts of abandoned sulphide mines - the example of Mathiatis Mine in Cyprus

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Abstract
The environmental impacts of the abandoned, open-cast sulphide mine of North Mathiatis (Cyprus) were investigated. In order to assess the pollution in the area, both soil and water samples were collected. More specifically, three water samples were taken from the crater lake and one from the mine pit above the level of the crater lake. The water in the crater lake was characterized as a calcium-magnesium-sulfur brine solution in the presence of high metal concentrations, and were also described as highly acidic (pH 2.93-3.04) with very high electrical conductivity (5690-5730 μS/cm). The water sample taken from the mine pit above the level of the crater lake was characterized as alkaline (pH=7.63) and, apart from lead (Pb), the concentration of all the other metals examined (Cu, Fe, Cr, Mg, Ca) are not considered elevated. Seven solid samples from the waste dumps were taken, and the sample analysis showed elevated concentrations of heavy metals and high level of acid mine drainage (AMD) was noted. Salt crusts were also observed at the ephemeral creeks within and outside the mine crater, which potentially threaten the adjacent ecosystem due to the high acidity and metal concentration, metals can be released with rain. It should be noted that, in order to examine the possible contamination of local aquifers, water samples from adjacent water wells should be taken and the communication of crater water with groundwater should be investigated. Finally, with the use of a thermal imaging camera (FLIR b50) the effect of the abandoned mine on soil and air temperature was examined. It was observed that where pyrite ore was left uncovered on the surface of the mine, in the absence of trees and cultivation, significantly higher temperatures were measured.

Keywords: sulphide mines; acid mine drainage; pyrite

Introduction

Copper mining in Cyprus dates back to ancient time until today. Copper in Cyprus is encountered in sulfide ore deposits and for that reason numerous mines were developed in areas where sulfide deposits were located [1]. North Mathiatis mine,located between the villages of Agia Varvara and Mathiatis in Nicosia district, is a typical example of an abandoned open-pit sulphide mine out of many in Cyprus. In the absence of legislation, mines are left abandoned without rehabilitation measures after the cessation of mining and as a result, the environmental impacts from mining still exist, influencing the surrounding area. North Mathiatis mine is abandoned since 1987 where large amounts of spoil heaps are left uncovered surrounding the open pit and are undergoing oxidation producing acidic leachates [2].

Acid mine drainage (AMD) is one of the main environmental impacts of sulphide mines. AMD is produced mainly when pyrite ore is left exposed on surface and is thereby oxidized by a combination of water, oxygen, and existing bacteria [3]. It is characterized by extremely low pH values and high concentrations of heavy metal ions, as well as sulfur ions, which pollute significantly large areas and surface/ground water systems [4-6].

The present study aims to characterize the extent of the environmental pollution at the abandoned open-cast mine of North Mathiatis, which is located between the villages of Agia Varvara and Mathiatis (Nicosia district, Cyprus).

Figure 1. North Mathiatis mine *(photograph taken March 2013)*

Materials and methods

In order to assess the pollution in the area, both soil and water samples were collected (2010). More specifically, three water samples were taken from the crater lake and one from the mine pit above the level of the crater lake (Figure 1). Water samples were analyzed by a private laboratory (Neolab Ltd; Chemical - Microbiological Laboratory of Foods, Water and Environment) for their pH, heavy metal content (Cu, Fe, Pb, Cr), SO_4^{2-}, Total Kjedhal nitrogen (TKN), NO_3^-, total phosphorous (TP), Ca^{2+}, Mg^{2+}, and for Boron. Liquid samples were also taken for comparison reasons from point MAT3 on April 2013 and June 2014. Samples were measured for their pH, conductivity and total dissolved solids (TDS) content. Also, in June 2014 a sample was taken from where the extracts of the waste piles were concentrated (MAT5).

Figure 1. Sampling points of water samples [7].

Soil samples were collected in April 2010 and the sampling points were chosen after considering the geology and topography of the area surrounding the mine pit, as well as the mineralogy and alteration intensity of the spoil heaps. The sampling points were chosen where it appeared that runoff from the site could potentially migrate toward the industrial and rural area of Agia Varvara. Sampling points were recorded using GPS. Samples were collected around the pit from the spoil heaps as well as from pyrite piles (Figure 2). During collection, the samples were described according to color, alteration intensity, visible minerals, and rock type. Samples were taken from the surface (0-10 cm). Seven samples were collected without using metal sampling equipment so as to avoid metallic contamination.

Soil elemental composition was obtained through X-ray fluorescence spectrometer (XRF). The solid samples were analyzed using a portable XRF Analyzer (ThermoScientific Niton XL2, Version 7.2). A total of 9 elements were identified (Fe, Cu, Pb, Zn, As, Ti, Sr, Mo and Se).

Furthermore, a thermal imaging camera (FLIR b50) was used to study the effect of the abandoned mine on soil and air temperature. Several locations of the abandoned mine were photographed so as to indicate in which areas of the mine is the environment affected by spoil heaps, the pyrite piles, the uneven growth of vegetation and the presence of minerals in the ponds. The thermographs were taken in April 2010. Thermography made in several parts of the abandoned mine (35 total points) and covering a wider area of the crater and ponds (see Thermography 4.1 - 4.7). All thermography were made during evening hours so as to reduce the impact of solar radiation reflected from the water of the crater. Temperature was measured (through thermography) at a height of 1.50 m above grade .

Figure 2. Image of the soil sampling points which were recorded with the use of GPS [7].

Results and discussion

Water samples analyses (Table 1) reveal that the pH of the water samples taken from the crater lake (MAT1-3) are consider as highly acidic (pH = 2.93-3.04) with very high electrical conductivity (5690-5730 μS/cm). From Table 2, it is noted that the pH of the crater (more specifically, sample MAT3) has decreased through the years from 3.04 to 2.82. Samples MAT1-3 are also characterized as a calcium-magnesium-sulfur brine solution in the presence of high metal concentrations. More specifically, high values of copper, iron and lead were measured. Considering that the primary and secondary minerals expected to be found in a massive sulfide ore deposit are pyrite (FeS_2), chalcopyrite($CuFeS_2$) and sphalerite (ZnS), the primary metals expected in leachate are iron (Fe), copper (Cu), and zinc (Zn).

Water sample (MAT4) taken from the mine pit was characterized as alkaline (pH=7.63) and, apart from lead, the concentration of all the other metals examined are not considered elevated. It should be noted that this point is several meters higher (≥30m) from the crater lake and is located at an area with abundant vegetation (pine and fig trees). This point is 10 meters below the road and is consider to be holding rain water. No pyrite ore was observed near point MAT4.

The sample collected at location MAT5 showed large amounts of leachates due to high precipitation, resulting to high leachability of metal ions. The pH is consider very acidic with high conductivity (Table 2).

Figure 3. Concentrated leachates from waste piles (MAT5) *(photograph taken June 2014)*

Table 1. Water sample analysis

parameter	**samples**				**unit**	**limit**
sampling point	MAT1	MAT2	MAT3	MAT4	-	-
depth (from the surface of crater water)	0.5	2	1.2	0.5	m	-
pH	**2.93**	**3.01**	**3.04**	7.63	-	6.5 – 9.5
conductivity	**5690**	**5730**	**5730**	1021	μS/cm	< 2500
copper (Cu)	**3.4**	**5**	**4.4**	0.14	mg/L	< 2
iron (Fe)	**710**	**1590**	**1510**	140	μg/L	< 200
lead (Pb)	**655**	**576**	**691**	**14**	μg/L	< 10
chromium (Cr)	20	10	30	20	μg/L	< 50
calcium (Ca^{2+})	294	405	520	150.4	mg/L	-
magnesium (Mg^{2+})	260	215.4	248.5	48.4	mg/L	-
sulphates ($SO4^{2-}$)	**1230**	**2140**	**4050**	220	mg/L	< 250
chlorine (Cl^-)	**416**	**391**	**472**	77.6	mg/L	< 250
boron (B)	**3.4**	**3.4**	**2.8**	0.3	mg/L	< 1.0
total hardness	1.8×10^3	1.9×10^3	2.32×10^3	574	mg/L $CaCO_3$	-
total Kjedhal nitrogen (TKN)	13.5	9.75	6	7.5	mg/L	-
nitrate (NO_3^-)	3.08	2.75	46.2	16.2	mg/L	< 50
total phosphorous (TP)	42	19.5	9	122.5	mg/L	-

Table 2. Water samples through time

	MAT3			**MAT5**
	2010	2013	2014	2014
pH	3.04	2.99	2.82	2.26
Conductivity	5730 μS/cm	7.58 mS/cm	8.91 mS/cm	19.67 mS/cm
TDS	--	4.85 g/L	5.70 g/L	12.59 g/L

During sampling, the soil samples were characterized visually with regard to alteration (Table 3). Samples collected from the spoil heaps were mainly characterized as limonitic [$Fe_2O_3 \cdot H_2O$] and hematitic [Fe_2O_3]. Samples collected from pyrite piles were characterized as fine-grained pyrite with quartz.

Table 3. Characterization of soil samples

Sample	Sample Type
MATH 1	Sample from the Spoil heaps. Limonitic yellow and grey clay. Hematitic oxidised lava rock.
MATH 2	Sample from the Spoil heaps. Limonitic yellow and grey clay. Hematitic oxidised lava rock.
MATH 3	Sample from the Spoil heaps. Limonitic yellow and grey clay. Hematitic oxidised lava rock.
MATH 4	Sample from the pyrite pile. Fine grained pyrite. Quartz.
MATH 5	Sample from the Spoil heaps. Limonitic yellow and grey clay.
MATH 6	Sample from the Spoil heaps. Limonitic yellow and grey clay.
MATH 7	Sample from the pyrite pile. Fine grained pyrite. Quartz.

The sample composition was measured for 9 elements and is presented in Table 4. In the absence of Cypriot legislation that directly concerns soil contamination, we searched for the allowable limits in force in other countries, and chose to compare our results to the Canadian standards [8]. All samples are rich in iron content (table 4) and confirm the presence of pyrite that was identified during visual description. The oxidation of pyrite (FeS_2) is a significant factor in the formation of AMD, an environmental problem of considerable concern. Pyrite is acid-insoluble sulfide mineral. Minerals such as pyrite (FeS_2; the most abundant of all sulfide minerals) are chemically (and biologically) stable in situations where both oxygen and water are excluded. However, upon exposure to both moisture and air (*e.g.*, following the fracturing and exposure of sulfide-containing mineral ores) sulfide minerals will oxidize spontaneously (reaction 1, 2) [9]:

$$FeS_2 + 7/2\, O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$
$$Fe^{2+} + ¼\, O_2 + H^+ \rightarrow Fe^{3+} + ½\, H_2O \qquad (2)$$

The soils collected from the pyrite piles (MATH4 and 7) contained higher concentrations of zinc in relation to the other samples, and above the permissible limits from the Canadian guidelines. Samples contain high concentrations of copper, arsenic and selenium, which are also above the limits for Canadian guidelines. Lead concentrations are above the limits for agriculture and residential-parkland soils. Furthermore, salt crusts were also observed at the ephemeral creeks within and outside the mine crater that may threaten the adjacent ecosystem due to the high acidity and metals that can be leached during a rain event. It should be noted that, in order to examine the possible contamination of local aquifers, water samples from adjacent water wells should be taken and the communication of crater water with groundwater should be investigated.

It should also be noted that during a study by Hudson-Edwards *et al.* (2005) concerning the North Mathiatis mine in Cyprus, samples of stream sediments and salt crusts were collected which indicated elevated concentrations in As, Cu, Pb, and Zn. Those authors suggested that, as in other mining-affected areas, soluble Fe sulfate minerals that form salt crusts control the potential mobility of As, Cu, and Zn, but there is evidence at N.Mathiatis that the Al and Mg sulfates may also play a role in heavy metals mobility. Overall, As and Pb appear to be less soluble than Cu and Zn, which is probably due to mineralogical factors and, possibly, the relative sorption of these elements on the Fe, Al, and Mg oxide and sulfate phases.

Table 4. XRF analysis of soil samples

Sample	Fe %	Cu ppm	Pb ppm	Zn ppm	As ppm	Ti ppm	Sr ppm	Mo ppm	Se ppm	Bal* %
MATH 1	24.6	330	ND**	120	ND**	2180	50	ND**	20	75.08
MATH 2	19	190	140	140	50	1880	140	20	50	80.6
MATH 3	24.71	390	ND**	60	ND**	860	ND**	ND**	ND**	75,095
MATH 4	12.31	690	200	3320	160	ND**	40	40	ND**	87,142
MATH 5	14	120	310	990	90	2370	90	30	ND**	85.08
MATH 6	15.54	190	110	ND**	60	2560	50	ND**	30	84,107
MATH 7	5.92	120	80	4060	30	940	30	30	ND**	93,428
Agriculture[1]	N.I.	63	70	200	12	N.I.	N.I.	5	1	N.I.***
Residential/Parkland[1]	N.I.	63	140	200	12	N.I.	N.I.	10	1	N.I.
Industrial[1]	N.I.	91	600	360	12	N.I.	N.I.	40	2.9	N.I.

**Bal: Non metalic elements*

***ND: Not Detected (below detection limit)*

****N.I. Not Included*

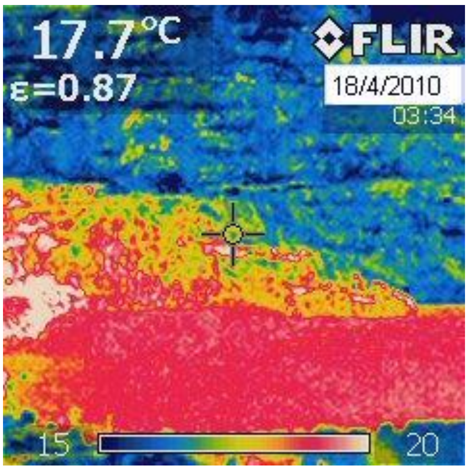
[1]: Canadian Environmental Quality Guidelines (2007) (http://st-ts.ccme.ca/)

Thermal Imaging

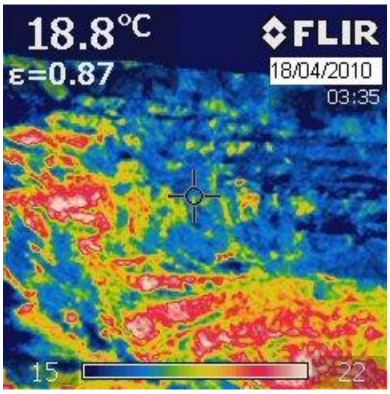
The effect of the abandoned mine on soil and air temperature was examined with a thermal imaging camera. It was observed that where pyrite ore was left uncovered at the surface of the mine, in the absence of trees and cultivation, significant higher temperatures were measured.

At several locations, the correlation between digital and thermographic imaging is very interesting. Most times the temperature difference is immediately visible without needing any specialized knowledge, such as photography and thermography (Figure 4 and Thermograph 1) which depicted the area east of the crater (see Figure 1, above the MAT3 sampling point). In Figure 4, pine vegetation is visible in the upper part of the photo and in the center of the picture the sulphurous pond and below the water of the crater is visible. Thermograph 1 shows exactly the same location, but with thermographic analysis. It can be concluded that the points shown vegetation, thermography record temperature from 15ºC to 17ºC, and where vegetation is missing, the soil temperature reaches to 21ºC, depending on the quality of soil and its components in ores. Similar observations can be made for all locations where thermographs were obtained (Thermograph 2 – 7).

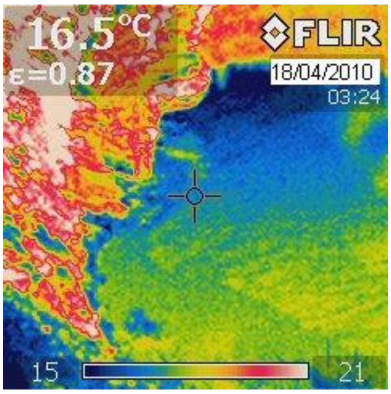
Figure 4. East side of the crater



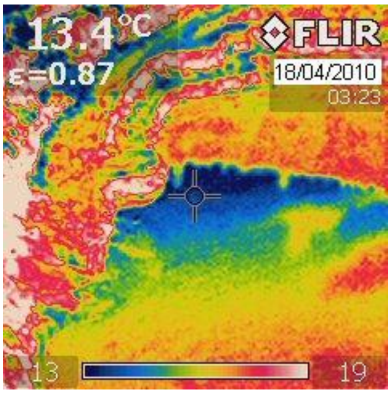
Thermograph 1. East side of the crater



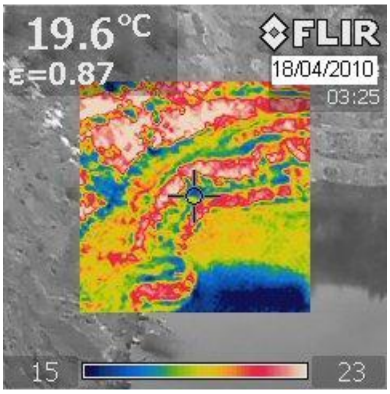
Thermograph 2. East side of the crater



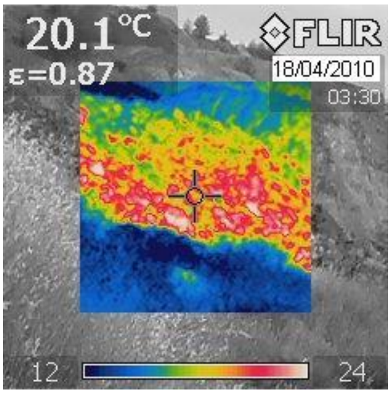
Thermograph 3. North side of the crater



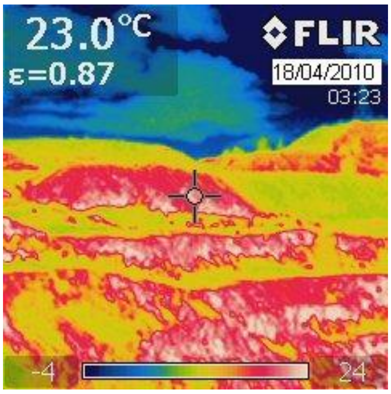
Thermograph 4. West side of the crater



Thermograph 5. South side of the crater



Thermograph 6. Sulphides ponds in North Side



Thermograph 7. Sulphides ponds in North

The thermographic images showed that, in locations where vegetation is observed, the soil temperature is in the range of 15-16ºC, while the crater water exceeds 18ºC and locally reaches up to 23ºC (Thermography 7). The water in the crater shows higher temperatures, as it is directly affected by the acidity and solar radiation. In spoil heaps, where various surface metallic ores are available, the temperature is locally increased. At locations were air temperatures were measured close to Agia Varvara village, the temperature was measured up to 3,1ºC higher than the area south of the mine (for Mathiatis village).

Conclusions

Acid mine drainage is produced in sulphide mines mainly by the oxidation of pyrite (FeS_2) and is a potential threat to water and soil pollution. In North Mathiatis mine, the crater lake is characterized as highly acidic (pH 2.93-3.04) with very high electrical conductivity and high metal concentrations. More specifically, the high concentrations of iron and low pH are typical characteristics of AMD. When AMD contacts waste dumps, elements are leached and are transported downstream as dissolved free ions creating an acidic toxic pond.

Solid samples from the waste dumps were taken, and the sample analysis showed elevated concentrations of heavy metals and high level of acid mine drainage (AMD) was noted. Salt crusts were also observed at the ephemeral creeks within and outside the mine crater which may threaten the adjacent ecosystem due to the high acidity and metals that can be leached to runoff during rainfall.

Finally, it should be noted that, in order to examine the possible contamination of local aquifers, water samples from adjacent water wells should be taken and the communication of crater water with groundwater should be investigated.

The use of a thermal imaging camera showed that abandoned mine has an effect on soil and air temperature. It was observed that where pyrite ore was left uncovered in the surface of the mine, in the absence of trees and cultivation, significant higher temperatures were measured. Also, the air temperature measurements showed (north side) that the temperature close to Agia Varvara village is higher up to 3,1^{o}C than Mathiatis village 350 meters to the south.

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References

1. Gavriel I., Kostarelos K., Stylianou M., Environmental Assessment of the Abandoned Sulfide Mine of Kokkinopezoula in Cyprus, 3rd International Conference on Hazardous Waste 2012, September 2012, Pages12-14, (Technical Univ. of Chania).
2. Hudson-Edwards K.A., Edwards S.J., Mineralogical controls on storage of As, Cu, Pb and Zn at the abandoned Mathiatis massive sulphide mine, Cyprus, Mineralogical Magazine, October 2005, Volume 69(5), Pages 695±706.
3. Johnson D.B., Hallberg K.B., The microbiology of acidic mine waters. Research in Microbiology Volume 154, 2003, Pages 466–473.
4. Nordstrom D.K., Advances in the hydrogeochemistry and microbiology of acid mine waters, International Geology Review, Volume 42, 2000, Pages 499–515.
5. Foucher, S., Battaglia-Brunet F., Ignatiadis I., Morin D., Treatment by sulfate-reducing bacteria of Chessy acid-mine drainage and metals recovery Chemical Engineering Science Volume 56, 2001, Pages 1639-1645.
6. Johnson D.B., Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. Water Air Soil Pollution: Focus, Volume 3, 2003, Pages 47– 66.
7. Google Earth, ¨Cyprus, Agia Varvara¨, 3870500.36N and 365531676.18E. 29th of June 2010, June 2014.
8. Canadian Environmental Quality Guidelines, 2007, (http://st-ts.ccme.ca/)
9. Stumm W., Morgan J.J., Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters, 3rd Ed. John Wiley and Sons, 1996, New York.