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Environmental impacts of unmanaged solid waste at a former base metal mining and ore processing site (Kirki, Greece)

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Abstract

The Kirki project aimed to identify, among the mining waste abandoned at a mine and processing plant, the most critical potential pollution sources, the exposed milieus and the main pathways for contamination of a littoral area. This was accompanied by the definition of a monitoring network and remedial options. For this purpose, field analytical methods were extensively used to allow a more precise identification of the source, to draw relevant conceptual models and outline a monitoring network. Data interpretation was based on temporal series and on a geographical model. A classification method for mining waste was established, based on data on pollutant contents and emissions, and their long-term pollution potential. Mining waste present at the Kirki mine and plant sites comprises (A) extraction waste, mainly metal sulfide-rich rocks; (B) processing waste, mainly tailings, with iron and sulfides, sulfates or other species, plus residues of processing reagents; and (C) other waste, comprising leftover processing reagents and Pb–Zn concentrates. Critical toxic species include cadmium and cyanide. The stormy rainfall regime and hilly topography favour the flush release of large amounts of pollutants. The potential impacts and remedial options vary greatly. Type C waste may generate immediate and severe chemical hazards, and should be dealt with urgently by careful removal, as it is localised in a few spots. Type B waste has significant acid mine drainage potential and contains significant amounts of bioavailable heavy metals and metalloids, but they may also be released in solid form into the surface water through dam failure. The most urgent action is thus dams consolidation. Type A waste is by far the most bulky, and it cannot be economically removed. Unfortunately, it is also the most prone to acid mine drainage (seepage pH 1 to 2). This requires neutralisation to prevent acid water accelerating heavy metals and metalloids transfer. All waste management options require the implementation of a monitoring network for the design of a remediation plan, efficiency control, and later, community alert in case of accidental failure of mitigation/remediation measures. A network design strategy based on field measurements, laboratory validation and conceptual models is proposed.

Keywords

Acid mining drainage, heavy metals, monitoring, bioavailability, toxicity, hazardous waste

Date received: 16 December 2009; accepted: 19 May 2010

Introduction

Mining waste classification

A mine site is usually a complex industrial system handling huge amounts of rock in order to extract from them a lower or marginal amount of valuable metals or minerals. It thus comprises two activities: extraction and ore processing. The sheer mass of the material handled implies that the valuable commodity is extracted or concentrated near the site, and most of the waste is disposed of nearby. The specificity of mining waste requires adapted regulations and standards (JRC, 2004; EU, 2006a). Applying standard industrial waste regulations to the mining sector would lead to economically

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unrealistic requirements, as well as inefficient solutions (Charbonnier, 2001; Symonds and COWI, 2001).

The mining waste present at most metal mine sites comprises three very different types of material.

A. Extraction waste, consisting of rocks with variable amounts of ore and other metals. Waste heaps are potentially hazardous through acid mine drainage (AMD), requiring adequate water management (JRC, 2004).
B. Final processing waste, or tailings, constituted mainly of rock particles, with variable amounts of residual metals, and various species, plus residues of processing reagents. Tailings contain significant amounts of bioavailable heavy metals and metalloids (Concas et al., 2006), but these may also be released in solid form into surface water through a tailings dam failure (Rico et al., 2008). The most important remedial step is an adequate dam and water management (JRC, 2004).
C. Hazardous industrial waste, comprising unused leftover processing reagents, metal concentrates and other ore-processing waste.

Mining waste impacts

The potential impacts and remediation options for these three categories varies greatly. Former mine sites are frequently sources of pollution many years after closure, especially for heavy metals and metalloids. Specific geochemical phenomena such as AMD and acid rock drainage (ARD) contribute to increase such environmental impacts. They may be mitigated, provided that adequate remediation measures are taken at the time of mine closure. In other cases, when a site is abandoned and left to itself and exposed to the environment, impacts may be worse, and evolve unfavourably with time. Other unfavourable factors include the proximity to exposed resources, such as groundwater, cultivated areas, urban settlements or seaside.

The case study

Such a situation is observed at Kirki (Thrace, 22 km NW Alexandroupolis; Figure 1), where mining and ore beneficiation for Cu, Zn and Pb ceased in 1995 and where no remediation action was taken (Michael and Dimadis, 2006a,b; Triantafyllidis et al., 2007; Liakopoulos, 2009). Tailings and impoundments were exposed to atmospheric conditions and their chemical, mineralogical, physical and geotechnical characteristics were affected. The climate, which can be an important destabilising factor, is harsh in the Kirki area, with hot and dry conditions during summer, and cold, rainy and windy days in the winter (temperate Mediterranean continental climate). The mean temperature in Alexandroupolis ranges from 8.5°C (January) to 30.1°C (August) (Romaidis, 2007). The range is even higher at Kirki due to the local foothills microclimate and the distance from the coast.

Drainage from the Kirki mine is collected by the Kirkalon brook, joining a small river, Eirini, near the plant (Figures 1, 2 and 3) which reaches the sea near Alexandroupolis through a cultivated plain overlying aquifers used for water supply.

A monitoring programme was implemented in 2005 by the Institute of Geology and Mineral Exploration (IGME), with the support of the European Union structural funds (Third Community support framework, Ministry of Development, Operational Programme "Competitiveness" (O.P.C.), project 65231). During the project, two reconnaissance missions were led by IGME and BRGM to test the feasibility of the implementation of on-site analysis within the monitoring programme. These tests provided enough data to classify waste types, identify the main pathways for emissions and to support the network design by conceptual models. The present paper is based on data and observations collected during these missions, along with regular monitoring data and observations gathered by IGME geoscientists (Michael and Dimadis, 2006a,b; Romaidis, 2007; Liakopoulos, 2009).

Materials and methods
Scope of the work

The study was focused on chemical impacts, and it aimed to geochemically characterise the sources and their emissions towards the environment. The impact itself on potential receptors was identified (presence and concentration of contaminants) in order to design a relevant monitoring network but the extent of environmental damage was not fully mapped. In addition to waste material, the main geochemical media (rocks, ores, soil, river sediment, surface and groundwater) were therefore sampled and analysed, with both laboratory and field techniques where possible.

Sampling strategy, conventional field methods and laboratory analyses

Surface and groundwater was sampled at 52 monitoring points, including private and public groundwater boreholes, an open pit lake, water drainage from the waste piles and the tailing dumps, seven newly installed groundwater wells near the processing plant area (Figures 2 and 3) and the main stream water from Kirkalon and Eirini brooks, at regular intervals during 2005 to 2007. Prior to water sampling the temperature, pH and electrical conductivity (EC) were measured on-site with portable instruments. Major elements in the water were analysed on raw unfiltered samples by wet chemical methods, mostly according to ASTM standards. Samples for multi-element analysis were filtered at 0.45 μm on site and preserved using ultra-pure HNO_3 in 250 mL
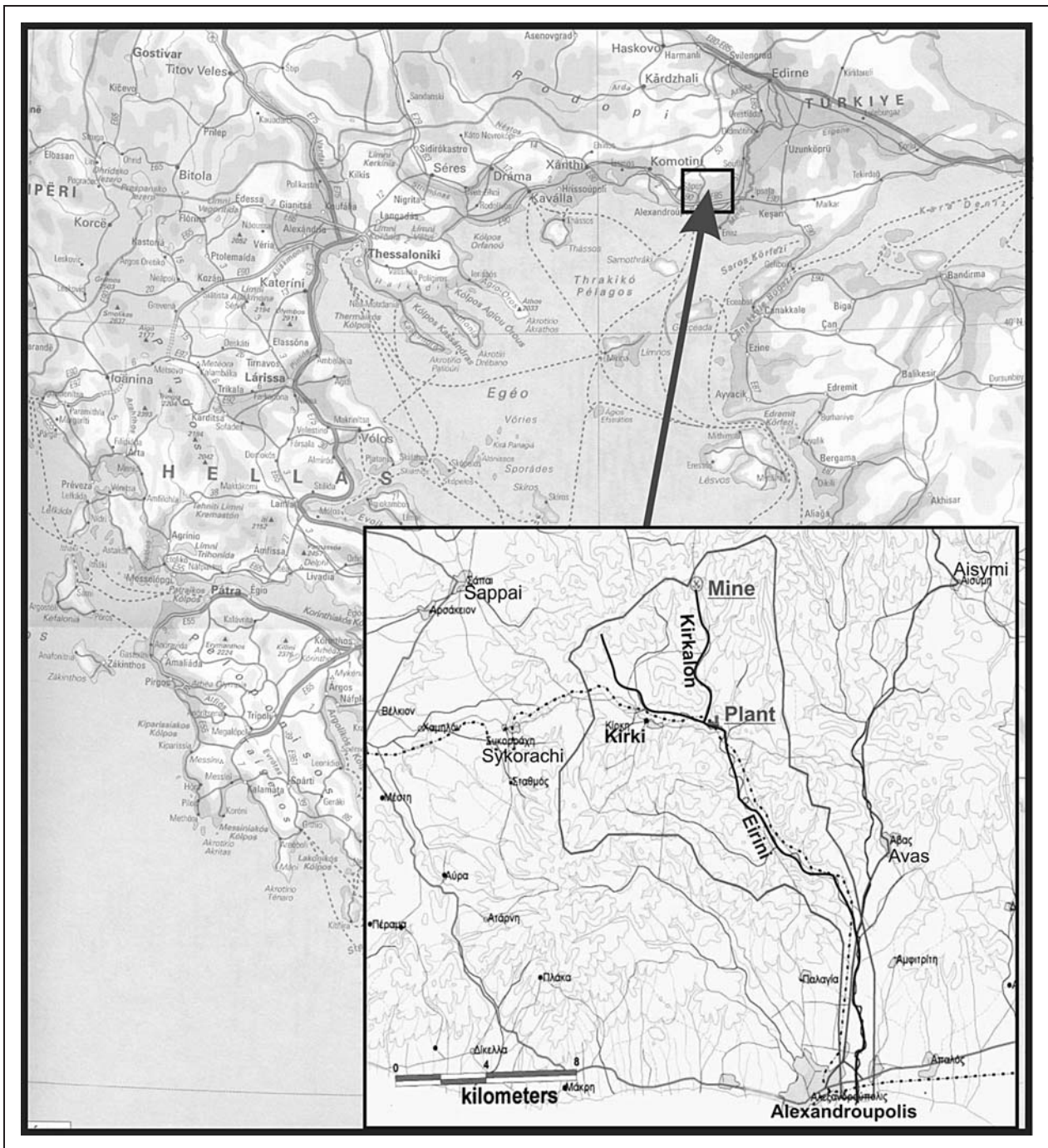
Figure 1. The Kirki mine area.

polyethylene bottles. Trace elements were analysed by ICP-MS (ASTM D5673:2003). Flow data were obtained on profiled sections using velocity measurements with a rotating element current meter (Romaidis, 2007).

Solid samples were analysed by a combination of ICP-AES and ICP-MS after aqua regia digestion.

Multiparametric probe for in-situ measurement of physico-chemical parameters

A multiparametric probe with depth sensor (Idronaut Ocean Seven 302) was used to perform chemical diagraphies of

water wells (pH, temperature, conductivity, Eh, dissolved O_2) (Lemière and Crouzet, 2006).

Anodic stripping voltammetry for on-site measurement of metals in water

Metal concentrations in water were determined near the site by square wave anodic stripping voltammetry (SWASV). Disposable printed microsensors (Palchetti et al., 2005) connected to a handheld instrument (PalmSens) allowed a lower limit of quantification of $5 \mu g L^{-1}$ for Cu, and limits for Cd and Pb close to $2 \mu g L^{-1}$. Validation was done within
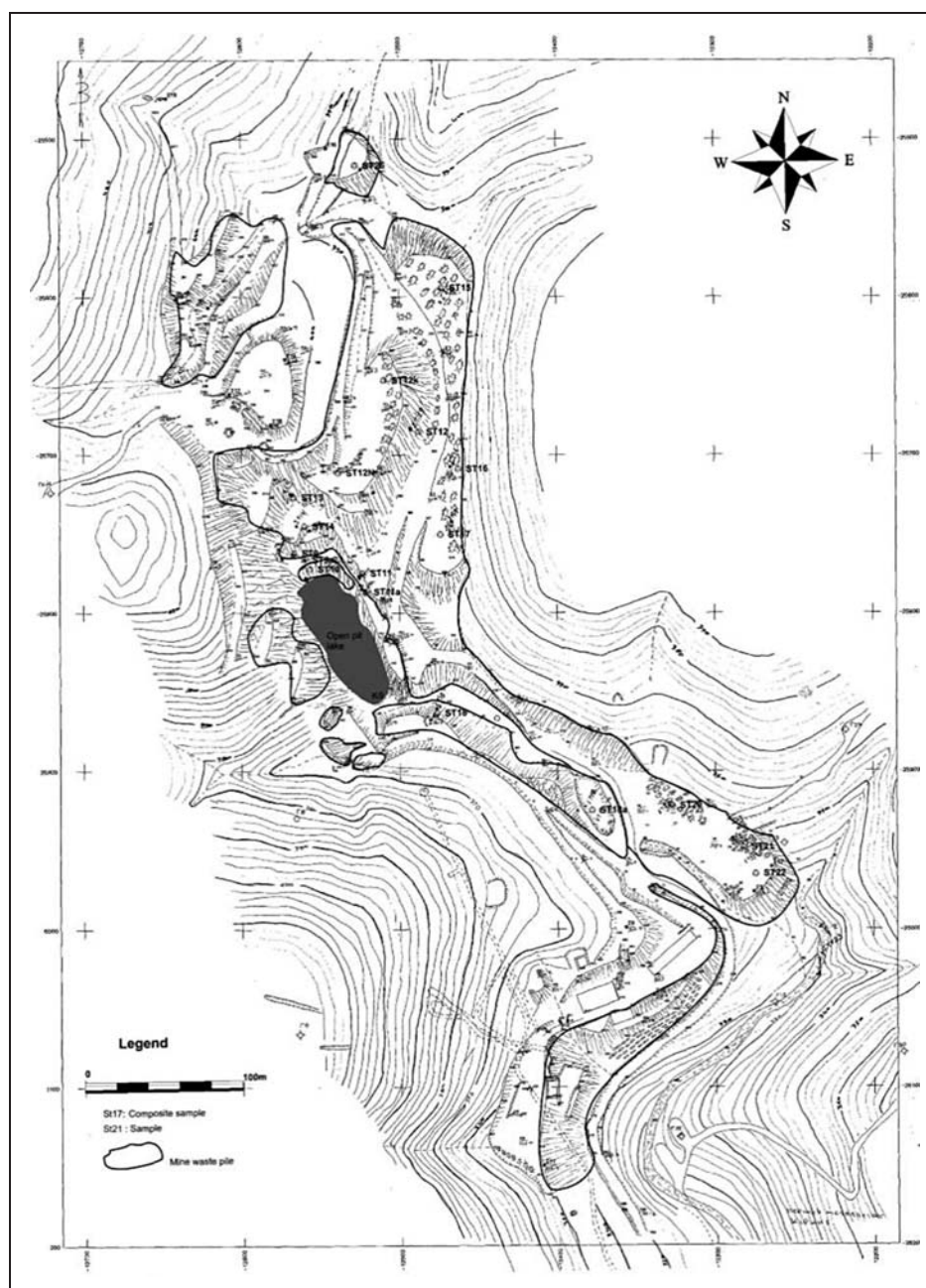
Figure 2. Total area disturbed by mining operations. The open pit lake and the extraction waste piles are delineated (Modified from Liakopoulos, 2009).

the framework of the European project SWIFT-WFD (SSPI-CT-2003-502492). The short distance allowed sample collection on demand. All samples were analysed on the day of collection or the next day (Lemière and Crouzet, 2006).

Field portable X-ray fluorescence for on-site measurement of metals in solids

The field portable X-Ray fluorescence (FPXRF) unit used for this mission was a NITON™ XLt792WY equipped with a X-ray tube (35 kV), Mo and Cu filters allowed the analysis of 22 elements (Mn, Fe, Co, Ni, Cu, Zn, As, Se, Pb, Hg, Rb, Sr, Cd, Ag, Sn, Sb; Cr, V, Ti, Sc, Ca and K) in optimum matrix conditions (Lemière and Laperche, 2006). It was selected for its analytical performance and its suitability for use in harsh field conditions.

The FPXRF unit was used either (a) directly in contact with the soil, sediment or rock target, (b) on-site on a roughly homogenised soil or sediment sample, or (c) in a near-site location where sample drying, sieving and milling was possible in order to allow sample preparation to be close as possible to laboratory conditions. Methods (a) and (b) were suitable for target identification and sample selection whereas method (c) was required for quantitative results (US-EPA, 1998).
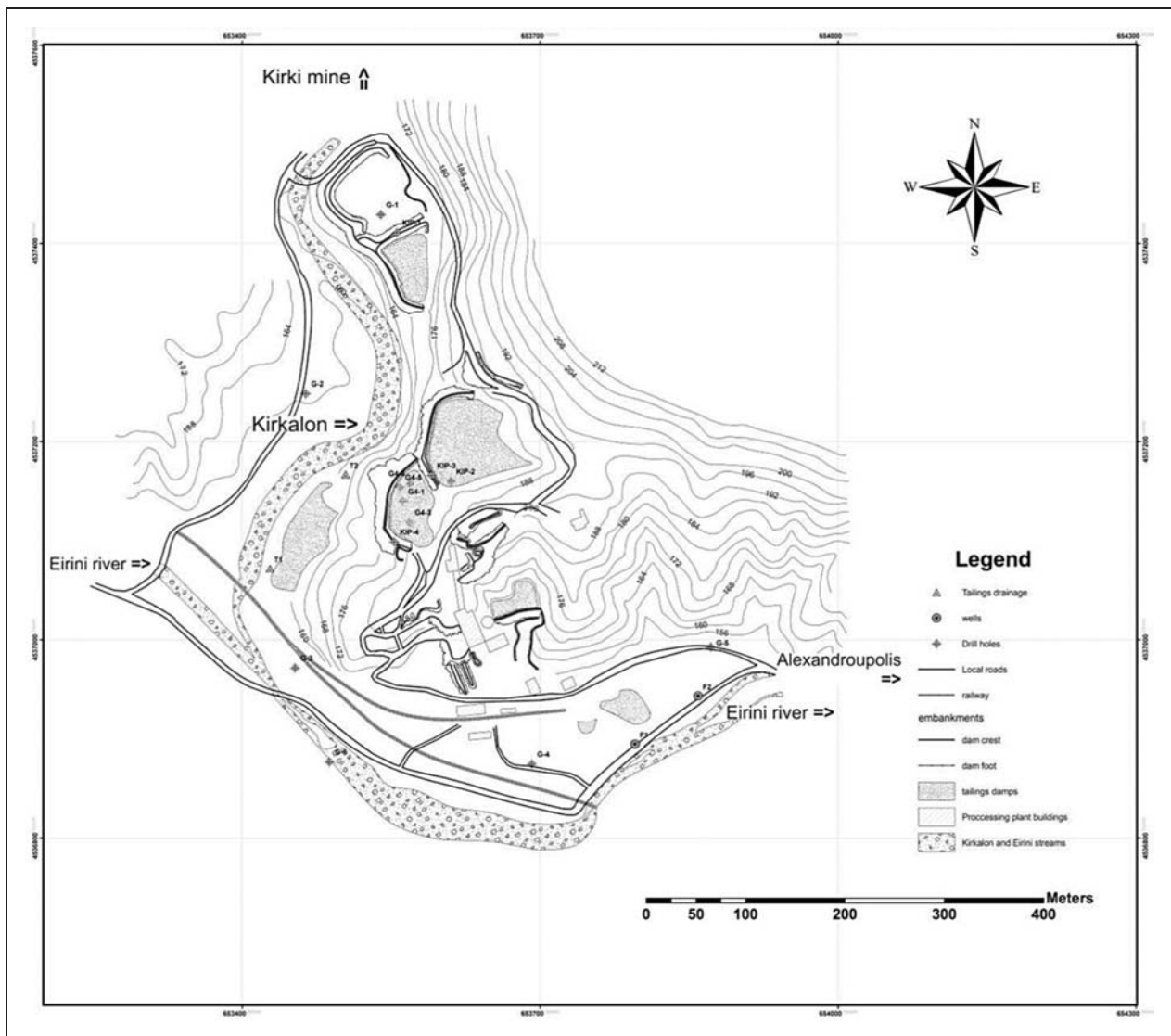
Figure 3. Map of Kirki processing plant area, indicating the position of the tailing dams. Modified from Michael and Dimadis (2006).

AMD potential evaluation

Acid drainage potential was assessed using the EPA toxicity characteristic leaching procedure (TCLP), which is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes, and the acid–base accounting (ABA) test. The latter is a screening procedure whereby the acid-neutralising potential (ANP) and acid-generating potential (AGP) of rocks, ore, mine waste and tailing samples are determined. The difference, net neutralising potential (NNP), and the ratio of neutralising potential (NPR) were calculated (CINAR and NTUA, 2007; Triantafyllidis et al., 2007; Papassiopi et al., 2009) in order to assess the acid-generation potential.

Data interpretation

Geochemical data were interpreted with the support of the PHREEQC model and geochemical maps were drawn using ArcGIS™. This provided a sound basis for the elaboration of conceptual models of pollutant transfer from the identified sources, including waste piles, towards potential receptors. The definition of a monitoring network is thus based on locating critical points along preferential transfer pathways, taking into account the actual geochemical processes such as neutralisation, precipitation or dissolution.

Results and discussion

Site topology and inventory of contaminants

The former mine (underground galleries and open pit) is located in a narrow valley in an area of low mountains (Figure 2). Base metals ores were extracted by underground mining and later by open-cast mining at Kirki. Open pit exploitation took place at an elevation of +430 to +345 m above sea level (Triantafyllidis and Skarpelis, 2006; Romaidis, 2007). The open pit has an ellipsoid shape and covers a total surface area of approximately 4700 m². A small lake, with a

Figure 4. General view of the open pit mine area. Mining waste dumped downstream and waste heap drainage escaping towards the brook.

depth varying between 2 and 8 m, fills the pit with water from rainfall and drainage (Liakopoulos, 2009; Papassiopi et al., 2009). Overflow occurs after heavy rains. Ferrous oxide precipitation occurs on the edge of the pit and along the overflow.

A total amount of 252 000 ton raw ore was extracted between 1973 and 1992. Extraction waste, including barren rock, low-grade ore and some high-grade ore, was stored as unmanaged piles in the immediate vicinity of the open pit, on the downstream course of drainage water (Figures 2 and 4). Waste piles are currently exposed to weathering processes that lead to the dissolution of sulphide and other minerals, the formation of efflorescences and crusts of sulphates such as alunite and natralunite (Liakopoulos, 2009) as well as AMD. The total lack of any vegetation and soil coverage on the sulphidic waste piles increases erosion rates. Both sheet and gully erosion can be so intense that fine-grained material, including sulphides and sulphates are washed away by rain storms.

The ores were beneficiated by flotation in a plant located 5 km south of the mine. A typical Zn concentrate composition was (in wt.%): Zn 50; Pb 1.5; Ag 0.012; As 0.12; Sb 0.02; Bi 0.01; Cd 0.60; Fe, 7.8; S total, 26.1 (S as SO_4, 3.0); Cu, 0.3; SiO_2, 1.7; Al_2O_3, 1.0; whereas a typical Pb concentrate composition was (in wt.%): Pb 55; Zn 5; Ag 0.07; Cu 2,5; As 1.3; Sb 0.33; Bi 0.95 and total S 17 (Michael and Exioglou, 2003). Processing waste materials, which are fine-grained tailings (ore flotation residues), were disposed of in eight basins around the plant, near the course of the Kirkalon and Eirini River (Figure 3) (Liakopoulos, 2009; Lemiere et al., 2009). The construction of the dams was initially performed by using uncompacted soil material, sand and conglomerates, arising from the neighbourhood talus cone and also from the excavation of the pits. Direct deposition of mud, in order to

increase the height of the embankments, is suspected in most of the tailings ponds (Michael and Dimadis, 2006b; Liakopoulos, 2009; Loupassakis and Konstantopoulou, 2009). The maximum height of the embankments varies from 5 to 10 m. The area of the tailing ponds varies from 400 to 8000 m^2, and the exact volume of their contents cannot be established without drilling or geophysical investigations (Loupassakis and Konstantopoulou, 2009). A tailings thickness of 2.60 to 3.25 m was measured in dam no. 4, by using sampling drill hole equipment (Liakopoulos, 2009). These tailings present a constant risk from physical instability (Konstantopoulou and Loupasakis, 2007; Loupasakis and Konstantopoulou, 2009) and spillage, with subsequent impacts on the surrounding rivers, soils and groundwater (Figure 5) (Liakopoulos, 2009).

Tailings contain lower but significant contents of ore elements (Cu, Pb, Zn, Ag, S) and may contain higher contents of unrecovered elements (Fe, Mn, Cd, Cr, Ni).

Contaminants from the mine were identified from ore samples and from the open pit pond water; they comprised Cu, Zn, As, Pb, Cd, Ni, Co along with anomalous levels of Mn, Fe and sulphate. Contaminants from the plant were identified from tailings samples and from water; they comprised Cu, Zn, Pb, Cd and anomalous levels of Mn, Fe and sulphate. These two contamination patterns, similar in essence to geochemical signatures, can be distinguished by the differential mobility of Zn, Cu and Pb.

Inventory and hierarchisation of contamination sources

The Kirki mine extraction wastes are strongly heterogeneous geological materials, and the particle sizes range from clay
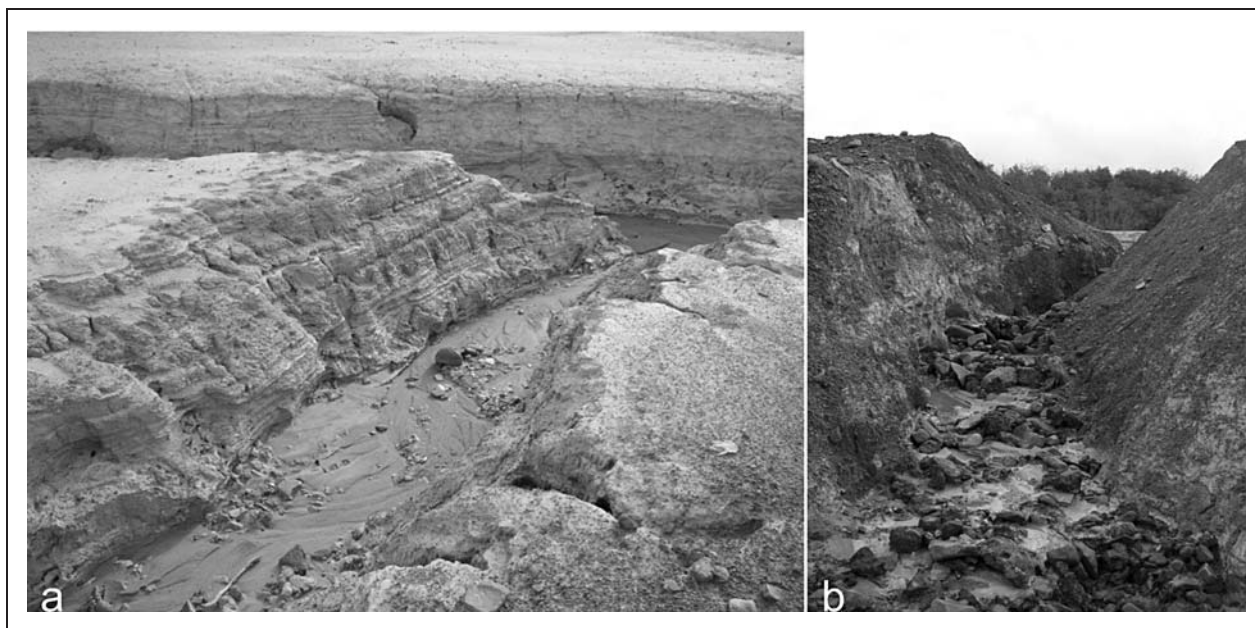
Figure 5. (a). Deep gully tailing dam erosion; (b) process waste (tailing) escaping through dam breach towards the river.

size to boulder size fragments. At the mine site (Figure 2), they include ore (observable at mine site exposures), extraction waste ('steriles', disposed of as waste dumps), and drainage sediment. The total surface of the operations area disturbed by mining, reached $77\,000\,m^2$ (Papassiopi et al., 2009) whereas the total volume of the waste pile was estimated by Michael and Dimadis (2006b) at $90\,000\,m^3$ (Figures 2 and 4).

Water-percolating waste dumps and open pit pond water also showed very high concentrations of contaminants (Table 1), along with strong acidity (pH 1 to 4) and salinity (especially sulphate, Table 1). This is a typical AMD situation. The mine area drainage was allowed to flow freely over and through the piles (Figure 4). The bottom drainage of the waste piles flows freely into the Kirkalon brook.

The majority of water data derived from the Kirki mine waste area were in the 'moderate acid/extreme metals' to 'near neutral/extreme metals' section of the Ficklin plot (Ficklin et al., 1992) shown in Figure 6, together with the data from drainage waters of the tailings dams. Waters from the open pit lake were plotted in the 'high acid/extreme metals' section, whereas data from underground mine gallery runoff (K4) and from the shallow aquifer, near to the plant plotted to the 'near neutral/extreme–high metal' section. The distribution of these high to extreme metal concentrations in acid as well as near neutral drainage waters implied that AMD was taking place at Kirki.

Tailings material contains significant contents from the environmentally important elements As, Cd, Cu, Pb, Zn, Mn, Cr, Ni and S (Table 1). This reflects the complex ore paragenesis (Michael et al., 1989). Along the main drill hole profiles (Figure 3: drill holes G4-1 to G4-4), the maximum concentrations (in $mg\,kg^{-1}$) for the elements listed before are: As 810; Cd 212; Cu 814; Pb 13748 (1.37%); Zn 19142 (1.9%); Mn 8947; Cr 210; Ni 159 and S 4.17% (Liakopoulos, 2009).

According to Papassiopi et al. (2009), the neutralisation potential to acid potential (NP/AP) ratio of the ABA test, varies from 0.0 to 1.6 for extraction waste, implying a minor to significant level of AMD risk, whereas for tailings the ratio varies between 0.0 and 0.2, implying a minor level of AMD risk only.

The predominant importance of the mine waste resulted from: (a) its larger volume (estimated $170\,000\,m^3$, about $400\,000$ ton, plus an extra $15\,700\,m^3$ of crushed ore near the mill, about $40\,000$ ton); (b) its permanent exposure to AMD which increases metal solubility by one to three orders of magnitude (Garralón et al., 1999). On the contrary, ore processing waste (tailings) represented a lower quantity (estimated $36\,500\,m^3$, about $80\,000$ ton), and they are less exposed to AMD. However, they represent a significant contamination source in solid form, as un-maintained tailings dams failure allows metalliferous tailings to be released to the Eirini river through breaches (Figure 5).

Contaminant mobility and bioavailability is higher in tailings than in ores or rocks (Concas et al., 2006). It may be further increased by the local climatic and hydrologic conditions, favouring oxidation and flushing through hydration–dehydration cycles (Kovacs et al., 2006).

Moreover, the migration and dispersion of trace metal elements such as Cd, Pb, Zn, Mn, Cu also happens due to erosion and mine run-off phenomena during heavy rainfall events, and due to the emission of air-borne particles during dry and windy periods.

Other waste comprises abandoned process reagents such as: xanthate, sodium sulphide (Na_2S), zinc sulphate heptahydrate ($ZnSO_4.7H_2O$), disodium metasilicate (Na_2SiO_3),

Table 1. Typical contents in heavy metals and metalloids for investigated locations

	Unit	Cu	Pb	Zn	Cd	As	Ni	Mn	S	pH	EC (μS cm^{-1})
Mine area											
Ore (1)	mg kg^{-1}	250 000	400 000	90 000	b	20000			250 000[f]		
Open pit water	μg L^{-1}	10 550	900	270 000	2350	6	1120	82 000	430 000[g]	2.7	2160
Downstream mine waste dumps											
Mine waste (dump)[a]	mg kg^{-1}	700	15 000	2000		1200			3000–20 000[k]		
Mine dump area	mg kg^{-1}	160	2700	6400	45	98	33	3400	4600		
Waste dump drainage	μg L^{-1}	4840	640	93 600	1120		864	129 000	430 000[g]	1.5–4	1700–2000
Mine brook water	μg L^{-1}	260	14	51 650	184	12	495	37 000	404 000[g]	7.3	1930
Brook sediment[a]	mg kg^{-1}	300	2200	18 000	c	100	50	29 000	250 000[g]		
Brook sediment	mg kg^{-1}	200	5000	11 000	175	140		1200	170 000[g]		
Plant area and downstream											
Concentrate[h]	wt. %	1.0	15.5	33.5	d	e			26.1		
Tailings[a]	mg kg^{-1}	257	6920	11 600		135		5160			
Tailings	mg kg^{-1}	295	6820	11 600	157	138	70	2800	15 000–20 000[m]		
Groundwater near plant	μg L^{-1}	6–20	j	9000–200 000	100–2700	< 20	50–400	700–10000	530 000[g]	5.3–6.9	1300–2380
River water near plant	μg L^{-1}	6–10	<40	2200–5400	26–72	j	15–100	1350–4200	55 000[g]	7.5–8.3	400–1100
River sediment near plant[a]	mg kg^{-1}	j	95	157		24		330			
Soil near plant[a]	mg kg^{-1}	80–240[a]	700–1200[a]	800–33000[a]	<250[a]	<100[a]		900–11000[a]			
Groundwater (irrigation)	μg L^{-1}	48	<5	340	4	<5	53	2150		7.2	708

[a]Estimated from semi-quantitative FPXRF data.
[b]No data available but estimated 30–3000 mg kg^{-1} from geochemical ratio.
[c]No data available but estimated 100–1000 mg kg^{-1} from geochemical ratio.
[d]No data available but estimated 0.1–1% from geochemical ratio.
[e]No data available but estimated 0.25–2.5% from FPXRF measurements.
[f]Estimated minimum contents from sulfide-bound metals.
[g]Calculated from sulfate.
[h]Mine statistics.
[j]Below analytical limits.
[k]Total S% varies between 0.34 and 1.94% of which SO$_4^{2-}$ is between 0.34 and 0.95%, and the remainder (0–1.15%) is sulfide (S) (0).
[m]Total S% varies between 1.48 and 2.09%, of which SO$_4^{2-}$ is between 0.22 and 0.24%, and the remainder (1.25–1.86%) is sulfide (S) (CINAR and NTUA, 2007).
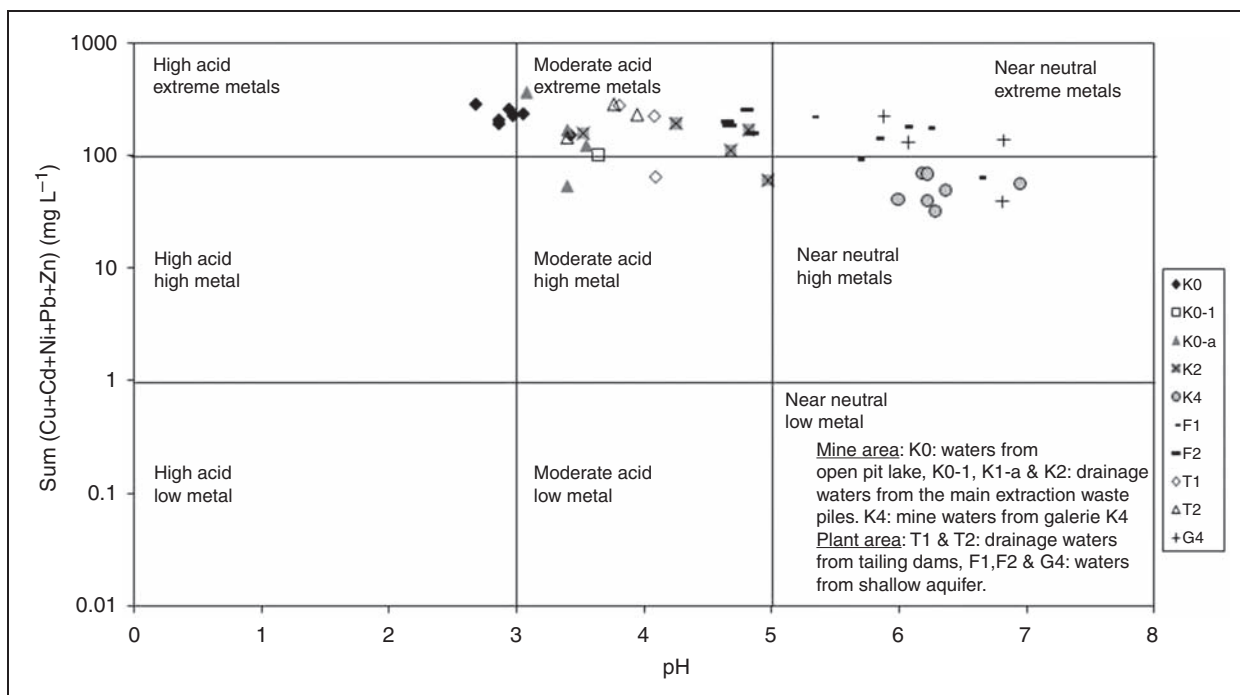
Figure 6. Ficklin diagrams of pH versus dissolved metal content in water samples collected from the Kirki Mine and the Kirki plant area.
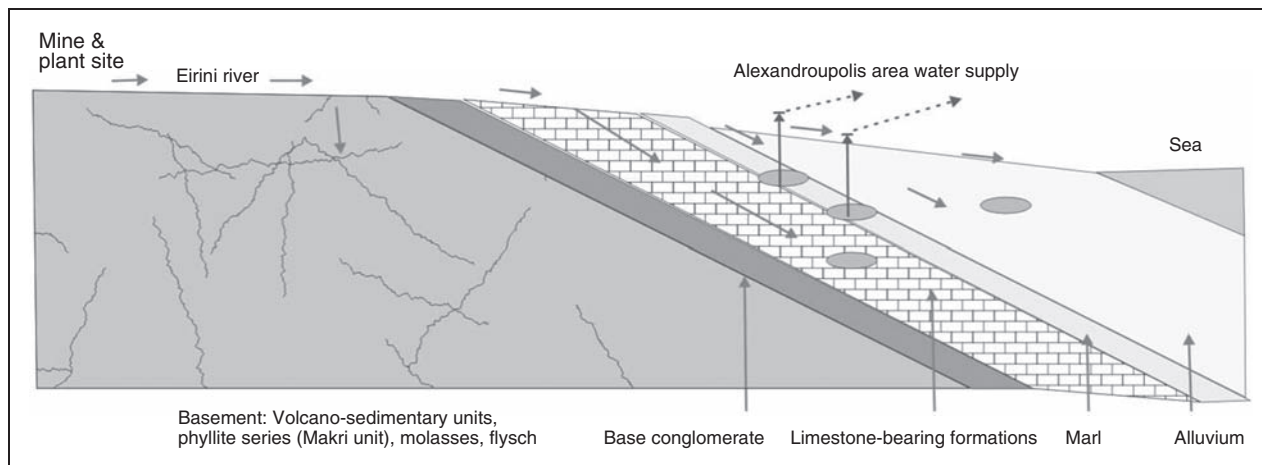

Figure 7. Conceptual model of receptor contamination by the mine and plant waste.

disodium carbonate (Na_2CO_3), cyanide compounds like 2-4 toluene diisocyanate (Liakopoulos, 2009), and possibly NaCN (Arrikas et al., 2007; Lemiere et al., 2009) plus flotation cake, ore concentrates and engine oil. Processing reagents and concentrates constitute an immediate source for contamination, due to their derelict condition, but most of it would no longer constitute a source once the heaps and barrels are removed.

Mapping of contamination receptors

Analyses of the above-mentioned contaminants in river water and sediments showed that mine and plant-related pollutions have significant impacts downstream until reaching the sea, 25 km from the mine site (Figure 7). The investigation for impacts in the catchment was much more detailed due to the use of field methods (FPXRF and voltammetry), and the option of immediate results allowed the sampling plan to be refined. The most significant points and samples were then subjected to laboratory analyses.

No permanent habitation, cultivated area or water resource use was observed between the mine site and the Eirini river, which collects all the site drainage (Figure 8). Local farming and grazing was observed near the former plant site, on the Eirini alluvial flats. Contamination was observed in soil and shallow groundwater (Table 1, Figure 9).

Groundwater monitoring investigations revealed that uncontrolled infiltration of the surface water along the
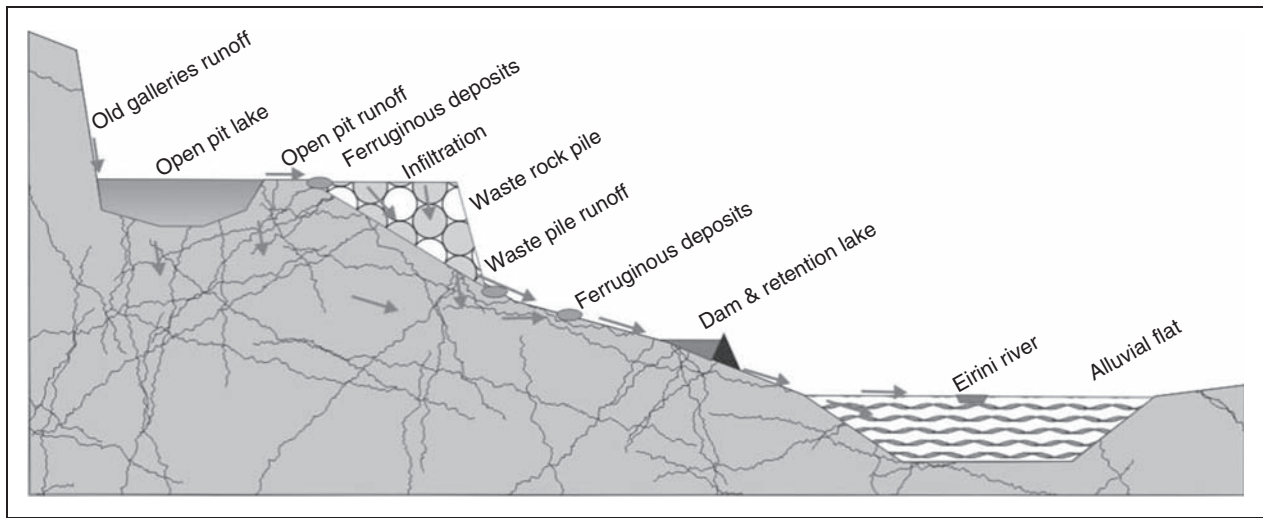
Figure 8. Conceptual model of contaminant emission by mine waste.
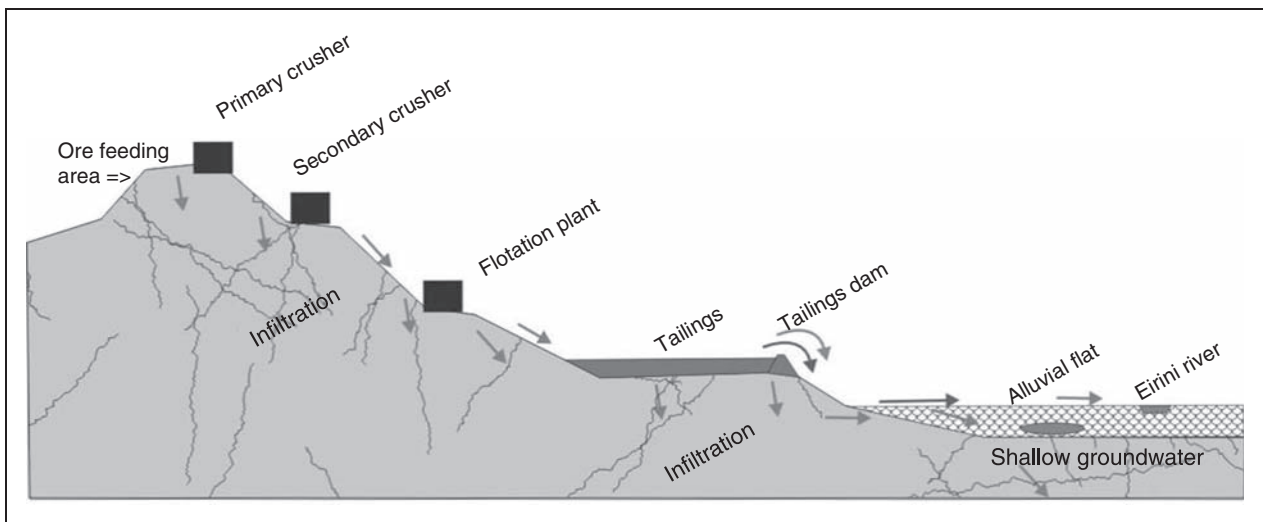
Figure 9. Conceptual model of contaminant emission by ore processing waste.

main pollution sources of the plant area (tailings ponds, plant facilities), allows pollutants to contaminate shallow groundwater (Liakopoulos, 2009).

Water contamination occurs in surface and shallow groundwater (aquifer) in a large area including the Kirkalon valley, the vicinity of the plant and in the Eirini valley some 100 m downstream of the processing plant, making it unfit for agricultural use due to surface and groundwater contamination.

However, the main potential receptors are located further down the Eirini valley, being the agricultural areas of the littoral plain and the underlying groundwater resources (Figure 7). The contaminated Eirini water may easily infiltrate through the karstic system and contribute to groundwater recharge.

The concentrations of toxic metals in the surface and ground waters varied widely from point to point at the study area (Table 1) but also from season to season (Liakopoulos, 2009). High concentrations of Zn, Mn, Cd, Cu, Ni and Pb were observed in water, especially from the mine and the plant area (Figure 10).

Based on the available data, the metal levels were nevertheless relatively low, below the Greek National drinking water standards, in the Eirini river, as well as at the Alexandroupolis water supply aquifers (Figure 10, Table 1), but careful monitoring of ore elements should be continued.

It is essential to guarantee a suitable water quality for the future. For this the littoral groundwater resources must be regularly monitored at least for As, Cd, Cu, Pb and Zn using high sensitivity methods, in order to warn if contamination by mine-derived pollutants builds up in the aquifers. If contamination is found to be increasing, a community alert system would be necessary.
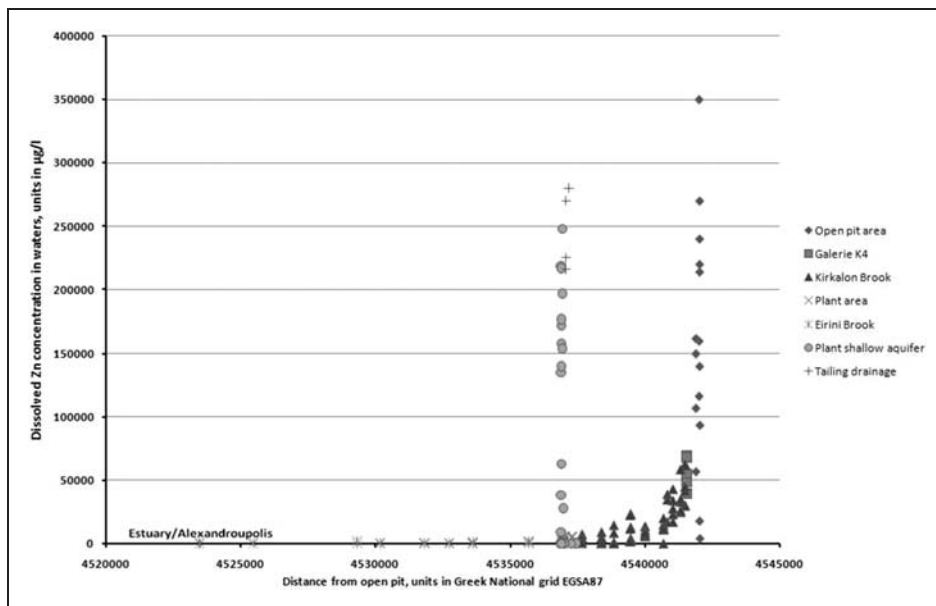
Figure 10. Dissolved Zn concentration in waters from the Kirki mine area.
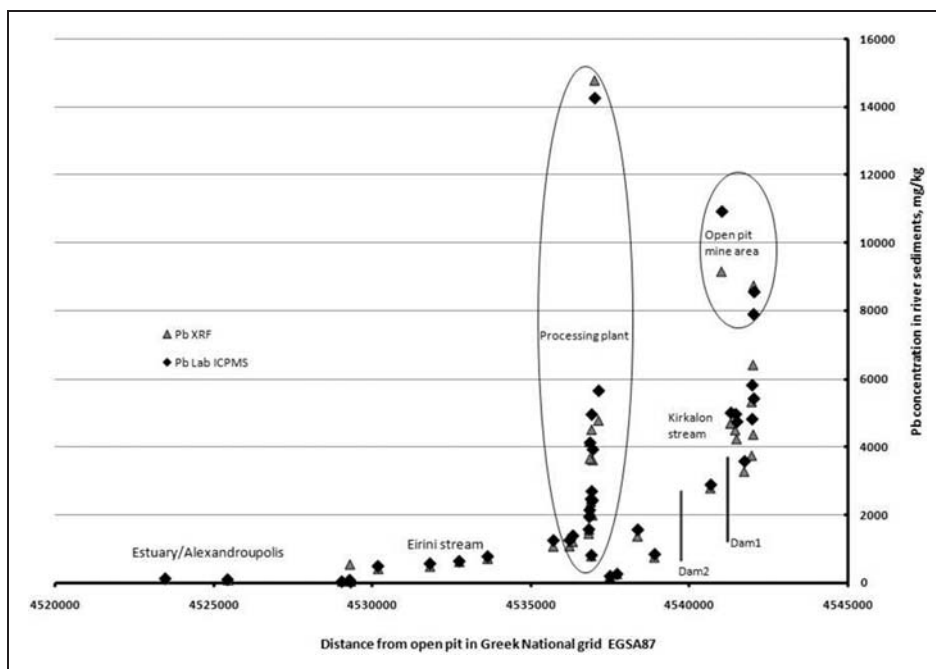

Figure 11. Pb Concentration in Kirkalon and Eirini streams sediments.

Last, it should be remembered that contaminated surface water and carried sediment end up in the Aegean Sea, with possible impacts on the marine life, which are not yet documented.

In the case of stream sediments, contamination occur at high levels in all Kirkalon stream sediments and drops gradually downstream of the plant in the first part of the Eirini course (Figure 11). The migration of contaminated sediment is controlled by the existence of two dams along the course of the Kirkalon brook.

Conceptual models for contamination from waste sources

At the mine site, the main contamination process is the exposure of oxidised metal sulphide and sulphate to rainfall and infiltration water. It occurs in the old mine galleries (runoff water), in the open pit (water pool) and in the extraction waste pile, where it is most efficient due to the fragmented state of the rocks. This is reflected by the lower pH of waste dump drainage. Dissolved Cu, Zn, Pb, As and Cd are

released in solute form to the mine brook, where neutralisation occurs mainly between the waste pile bottom and the dam (Figure 8). Metal movement continues downstream in solid form, as precipitate or sediment. Mine emissions reach the Eirini river near the plant site.

At the plant site, waste leaching by rainfall is also active on ore stockpiles, on concentrate and on tailings. However, contaminant concentrations in solute form are much lower due to the near neutral pH values and absence of widespread AMD. They are nevertheless high enough to affect soil and shallow groundwater at the plant site (Figure 9), although the exact contribution of mine pollution and of plant pollution cannot be specified. The most important mass of contaminants is released in solid form, as direct tailings discharges to the river during storm rains (Figure 5).

Most of the contaminants released to the Eirini river, both from mine and plant origin, are in solid form. They can be flushed to the sea as such, but they may also accumulate in sediment pools and release Cu, Zn, Pb, As and Cd to the river water by redissolution, allowing further contamination of surface and groundwater resources (Figure 7).

The gradual decrease of the metal concentrations in solution, from the source points to the potential targets is due to: (1) neutralisation of acid waters at runoff; (2) dilution by unaffected stream waters, both of which increase pH values; and (3) subsequent precipitation of Fe and Al phases (Liakopoulos, 2009).

Waste classification, mitigation and remediation options

Mining waste present at the Kirki mine and plant sites comprises all of the categories mentioned above.

A. Extraction wastes mainly constituted of silicoaluminate rocks with iron and base metal sulphides, which are a major source for AMD (seepage pH 1 to 2). It is open to percolation; hence the only mitigation option is accelerated neutralisation of its bottom drainage, to prevent acid water accelerating the transfer of heavy metals and metalloids to the environment. Options for remediation are focused on water and drainage control. The construction of diversion channels for the main upstream brooks (e.g. Kirkalon and tributaries), in order to minimise direct rain-water percolation into the waste piles, is of first priority and should be investigated in detail. Downstream drainage neutralization might be achieved by filling the existing dam (Figure 8) with crushed limestone. However, this will leave the brook exposed to metal contamination. It is thus necessary to immediately prevent any use of its water (drinking, cattle breeding or irrigation), and to monitor water quality at the junction with the Eirini river.

B. Tailings, mainly constituted of rock particles, with iron and bioavailable base metals, including minor but significant amounts of toxic elements such as Cd and As (EU, 2006b). They may be also released in solid form towards surface water through uncontrolled dam failure. The most urgent remediation step is therefore dam consolidation. The remaining flotation mud found inside the processing plant, the dispersed mud around the tailing dams area and the river sediments from Kirkalon and Eirini streams, in the immediate vicinity of the existing tailings dams, should be carefully removed and collected into one of the existing tailing dams for storage.

C. Leftover processing reagents such as cyanide or xanthate, as well as Pb–Zn concentrates and other ore processing wastes abandoned in open air. These represent immediate and severe chemical hazards, localised in a few spots, and must be dealt with urgently by careful removal, as the recent cleaning operations completed only a very partial removal.

Before any remediation measure takes place, a detailed risk evaluation study should be initiated. A careful planning of mitigation actions is required, as waste removal and confinement may bring efficient options whereas improperly managed AMD may ruin any remediation efforts and lead to continuous pollution (Unruh et al., 2009).

Emissions monitoring should be performed by regular analyses of drainage, brook and river water downstream from the mine to Alexandroupolis town. This should be complemented by receptor monitoring of groundwater and soil near the plant and in the Alexandroupolis area (Lemière and Crouzet, 2006; Lemière and Laperche, 2006).

A community alert system should provide early information on emission peaks for Cd and other metals in the river water. This may be achieved by a network of rainfall recorders, pH-conductivity probes and flow sensors.

Conclusions

Two main types of abandoned mine waste are present at the Kirki former mining and ore processing site, and they currently present major environmental hazards for water and soil resources in the Alexandroupolis region, especially Cd and As contamination.

Mine extraction waste contributes through AMD and leaching, whereas ore processing waste (tailings) is also released in solid form. The former cannot be directly remedied economically as such and the resulting water contamination has to be mitigated in the drainage itself. Water contamination may be reduced by neutralisation, preferably with large-scale passive methods such as crushed limestone beds. The latter can be remedied through proper dam management and confinement. Other options such as mine backfill are available but would require adequate risk evaluation.

The main potential impacts are the contamination of surface water, soil and groundwater downstream of the plant facilities, especially the littoral groundwater used for drinking and irrigation purposes. This may require a community alert network if the present contamination of the so-far unused surface water affects the groundwater resources of the littoral plain in the future.

The identification of the contamination sources (waste) and targets (water, soil), the definition of pathways and conceptual models, and the design of a monitoring network were significantly easier and more efficient due to the availability of field methods (e.g. FPXRF, voltammetry). This strategy does not replace, but does improve, the traditional approach with laboratory analyses, and helps to keep costs under control.

Acknowledgements

References

Arrikas K, Asfahani N, Nowak A and Goetz D (2007) The Kirki mine in Evros Prefecture, NE Greece, and considerations on the environmental impact. *Mining and Metallurgical Annals* 17: 21–50 & 51–69.

Charbonnier P (2001) *Management of mining, quarrying and ore-processing waste in the European Union*, Final report to DG ENV on Mining Waste in the EU, BRGM report RP50319-FR. http://ec.europa.eu/environment/waste/studies/mining/0204finalreportbrgm.pdf Accessed 10 December 2009.

CINAR SA and NTUA (2007) Test results of environmental geochemical characterization of samples from the Kirki mine area. Unpublished IGME internal report, project 65231. IGME—Institute of Geology and Mineral Exploration, Athens, Greece.

Concas A, Ardau C, Cristini A, Zuddas P and Cao G (2006) Mobility of heavy metals from tailings to stream waters in a mining activity contaminated site. *Chemosphere* 63: 244–253.

EU (1991) Council Directive 91/689/EEC of 12 December 1991 on Hazardous Waste. Brussels, Belgium: The Council of the European Union.

EU (2006a) Council Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the management of waste from extractive industries and amending Directive 2004/35/EC (in short: MWD). Brussels, Belgium: The Council of the European Union.

EU (2006b) Directive 76/464/EEC of 4 May 1976 on pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (OJ L 129, 18.5.1976, p. 23). Directive as last amended by Directive 2000/60/EC. Brussels, Belgium: The Council of the European Union.

Ficklin WH, Plumlee GS, Smith KS, and McHugh JB (1992) Geochemical classification of mine drainages and natural drainages in mineralized areas. In: Kharaka, Y.K. and Maest, A.S. (eds): *Proc. of Water-rock Interaction: Seventh International Symposium on Water-Rock Interaction*, Park City, Utah, 13–18 July, 1992, Volume 1, pp. 387–384. A.A. Balkema, Rotterdam, The Netherlands.

Garralón A, Gómez P, Turrero MJ, Sánchez M and Melón AM (1999) The geochemical aspects of toxic waters retained in the Entremuros area (Spain). *The Science of the Total Environment* 242: 27–40.

JRC (2004) *Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities*. Sevilla, Spain: Joint Research Centre, European Commission.

Konstantopoulou G, and Loupasakis C (2007) *Geotechnical Stability Study of the Tailings Ponds of the Kirki Mine*. Evros Prefecture. Unpublished IGME internal Report. IGME—Institute of Geology and Mineral Exploration, Athens, Greece.

Kovacs E, Dubbin WE and Tamas J (2006) Influence of hydrology on heavy metal speciation and mobility in a Pb-Zn mine tailing. *Environmental Pollution* 141: 310–320.

Lemière B, and Crouzet C (2006) Test of monitoring tools for mining and industrial environmental applications on the Kirki mining area (Greece) – Phase 2. Unpublished BRGM report RC-55029-FR, 48 pp., 2 appendixes.

Lemière B, and Laperche V (2006) Test and feasibility of the implementation of monitoring tools for mining and industrial environmental applications on the Kirki mining area (Greece). Unpublished BRGM report RC-54499-FR, 102 pp., 5 appendixes.

Lemiere B, Laperche V, Crouzet C, Lassin A, Liakopoulos A, Michael C, Drougas I, and Romaidis I (2009) Geochemical investigations in view of the implementation of a monitoring system at a former base metal mining and ore processing site (Kirki, Thrace, Greece). In Proc. of Third AMIREG International Conference (2009): Assessing the Footprint of Resource Utilization and Hazardous Waste Management, Athens, Greece, pp. 253–257.

Liakopoulos A (2009) Environmental study of the former Kirki mines area. Pollution extension and proposed abatement measures. Unpublished IGME internal report. IGME—Institute of Geology and Mineral Exploration, Athens, pp. 227, 2 appendixes.

Loupasakis C and Konstantopoulou G (2009) Safety assessment of abandoned tailings ponds: an example from Kirki mines, Greece. *Bulletin of Engineering Geology and the Environment*, in press.

Michael C, Constantinides D, Ashworth K, Perdikatsis V and Demetriades A (1989) The polymetallic ore mineralization of the Kirki area, Alexandroupolis district, Northeast Greece. *Geologica Rhodopica* 1.

Michael K, and Dimadis E (2006a). Geological study of the area around the Kirki beneficiation plant. Unpublished IGME internal report. IGME—Institute of Geology and Mineral Exploration, Athens, Greece.

Michael K, and Dimadis E (2006b). Results of geological mapping in scale 1: 25.000 in the catchment area of "Eirini" stream. Unpublished IGME internal report. IGME—Institute of Geology and Mineral Exploration, Athens, Greece.

Michael K, and Exioglou D (2003). Inventory of past mining activities in the Eastern Rodope area. Unpublished IGME internal Report. IGME—Institute of Geology and Mineral Exploration, Athens, Greece.

Palchetti I, Laschi S and Mascini M (2005) Miniaturised stripping-based carbon modified sensor for in field analysis of heavy metals. *Analytica Chimica Acta* 530: 61–67.

Papassiopi N, Mylona E, Xenidis A, Paspaliaris I, Liakopoulos A, Angellatou V, and Drougas J (2009) Assessment of major acid generation sources in the mining site of Agios Filippos, Kirki, GR. In: Proceedings of 3rd AMIREG International Conference (2009): Assessing the Footprint of Resource Utilization and Hazardous Waste Management, Athens, Greece, pp. 333–338.

Rico M, Benito G, Salgueiro AR, Diez-Herrero A and Pereira HG (2008) Reported tailings dam failures – A review of the European incidents in the worldwide context. *Journal of Hazardous Materials* 152: 846–852.

Romaidis I (2007) Preliminary hydrogeological study of the Kirki mines area. Unpublished IGME internal Report. Institute of Geology and Mineral Exploration, Athens.

Symonds and COWI (2001) *A Study on the Costs of Improving the Management of Mining Waste*. Final Report to DG ENV on Mine Waste Costs. http://ec.europa.eu/environment/waste/studies/mining/mining_cost.pdf Accessed 10 December 2009.

Triantafyllidis S and Skarpelis N (2006) Mineral formation in an acid pit lake from a high-sulfidation ore deposit: Kirki, NE Greece. *Journal of Geochemical Exploration* 88: 68–71.

Triantafyllidis S, Skarpelis N and Komnitsas K (2007) Environmental characterization and geochemistry of Kirki, Thrace, NE Greece, abandoned flotation tailing dumps. *Environmental Forensics* 8: 351–359.

Unruh DM, Church SE, Nimick DA and Fey DL (2009) Metal contamination and post-remediation recovery in the Boulder River watershed, Jefferson County, Montana. *Geochemistry: Exploration, Environment, Analysis* 9: 179–199.

US-EPA (1998) EPA Method 6200. Field portable X-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment. In: *Test Methods for Evaluating Solid Waste*, 3rd edition (SW-846). With promulgated revisions. US Environmental Protection Agency (EPA), http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/6200.pdf (December 10, 2009).