Geochemical investigations in view of the implementation of a monitoring system at a former base metal mining and ore processing site (Kirki, Thrace, Greece)

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ABSTRACT

Mining sites are usually sources of metal pollution many years after closure. Specific geochemical phenomena such as acid drainage contribute to an increase of environmental impacts, especially if remediation measures were not taken at the time of mine closure (Bird et al., 2005). When a site is left exposed to the elements, pollution may arise from unmanaged waste piles, mine runoff water and tailings.

The implementation of a reliable monitoring system is required to assess risks for the exposed resources (groundwater, cultivated areas, urban settlements or littoral), until the site is remediated. Monitoring data are essential to design remediation works.

The monitoring network is designed using water, sediment or soil quality data along time at the critical points of the pollution transfer model.

Traditionally, such points are selected from a large number of sampling points and laboratory analyses (baseline data). This is both expensive and lengthy.

IGME followed an alternative route at Kirki, where mining and ore beneficiation for copper, zinc and lead ceased in 1995, and no remediation was undertaken.

A baseline monitoring program was implemented in 2005 with the support of the European Union, incorporating field analysis campaigns to improve its efficiency (heavy metals in water by polarography, in solids by portable XRF and multiparametric probes).

This allowed to identify quickly pollutant variation ranges, emission or attenuation points, and to design conceptual transfer models. Field techniques were particularly efficient to design an optimised monitoring network, by allowing an immediate feedback between results, investigations and sampling. They do not substitute to laboratory techniques, but optimise their use for a better representativity of phenomena. Examples of critical points include:

- neutralisation fronts for acid mine drainage, and metal precipitation sites,
- separation between rainfall recharge and contaminated aquifer in shallow wells,
- migration distance of each contaminant in sediments within the catchment.

The monitoring plan provides key data for remediation options, and for the design of a community alert system.

1. INTRODUCTION

Mining sites are one of the largest sources of metal pollution, by nature, and because they are among the largest industrial sites. The permanent nature of their imprint (works, waste) implies that this pollution may continue, or even begin, many years after closure. Specific geochemical phenomena such as acid drainage contribute to an increase of environmental impacts, especially if remediation measures are not taken at the time of mine closure. When a site is left exposed to the elements, pollution may arise from unmanaged waste piles, mine runoff water and tailings.

The European Union paid particular attention to the management of mine sites, active and closed, after major recent accidents (Los Frailes, Spain; Baia Mare, Romania, Rico et al., 2008) in mining and waste disposal sites hosting hazardous waste stocks, that threatened seriously water resources. This attention was reflected in regulations (Water Framework and Mining Waste Directives, European Parliament and Council, 2000; 2006) and reference documents (JRC, 2004).

These documents attribute a large importance to monitoring schemes, especially as remediation of mining sites generally does not guarantee the absence of future pollution.

Monitoring may be achieved by periodic sampling trips or by on-site measurement of the physico-chemical and chemical evolution of sources, vectors and exposed resources. Both approaches may be complementary as field methods have a quick responce, allowing sample selection, while lab methods are the only ones to provide full analytical quality.

2. SITE LAYOUT

At the mine site of Kirki (Thrace, 22 km NW Alexandroupolis, Arikas, 1979 Fig. 1), mining and ore beneficiation for Cu, Zn and Pb ceased in 1995 and no remediation action was taken since then.

A reconnaissance monitoring program was implemented in 2005 by IGME (Michaels and Dimadis, 2006a, b; Cinar and EMP, 2007; Romaidis, 2007; Liakopoulos 2009; Liakopoulos et al., 2009), with the support of the European Union structural funds (3rd Community support framework O.P.C.). During the project, two focused geochemical missions were led by IGME and BRGM (Lemiere and Crouzet, 2006; Lemiere and Laperche, 2006) to test the feasibility of the implementation of on-site analysis within the monitoring program. The present paper is based on data and observations collected during these missions, along with regular monitoring data and observations gathered by IGME geoscientists.

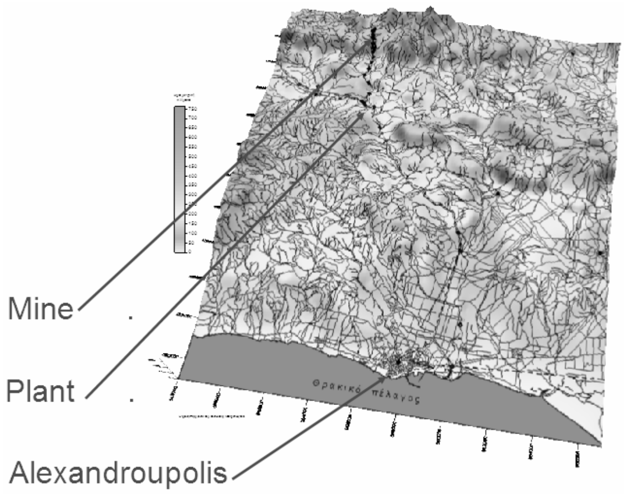

Figure 1: Geographic location of Kirki mine & plant.

3. METHODS

3.1 Laboratory

Geochemical analyses for water samples were done at the IGME laboratories (Xanthi) for major elements, while trace elements were analysed at the IGME laboratories (Paiania) on filtered and acidified samples by ICP-MS.

Analyses for solid samples were done by OMAC (Ireland) by ICP/AES and ICP/MS after aqua regia digestion.

3.2 Field

Key parameters (pH, EC, ORP) were determined on field using handy meters. Groundwater profiles were established with an Idronaut OCEAN SEVEN 302 multiparametric probe. Water flow data were obtained using a rotating element current meter on gauged sections.

A selection of samples was analysed on site for Cu, Pb, Zn, Cd and As by SWASV (Square Wave Anodic Stripping Voltammetry) on printed electrodes (Palchetti et al., 2005). A recent review (Buffle and Tercier-Waeber, 2005) of voltammetric applications confirmed the interest of the method.

Site investigations for heavy metals and metalloids (Cu, Pb, Zn, Cd, Mn, As and other elements) were performed with a FPXRF spectrometer (NITON™ XLt792WY). This instrument was used also for on-site analyses of dried, milled and homogeneised samples.

Table 1: Geochemical data, mine area.

Media	Ore	Open pit water (July)	Mine waste (dump)	Waste dump drainage	Mine brook water
Unit	g/kg	µg/L	mg/kg	µg/L	µg/L
Cu	250	10550	700	4840	260
Pb	400	900	15000	640	14
Zn	90	270000	2000	93600	51650
Cd		2350		1120	184
pH		2.7		1.5 - 4	7.3

Detailed descriptions are given in Lemiere and Crouzet (2006), and Lemiere and Laperche (2006).

3.3 Data processing

Field and lab data were consolidated with GPS coordinates using ArcGIS 9 mapping database software. Water geochemical interpretation was supported by PHREEQC modelling.

4. POLLUTION SOURCES, PATHWAYS, TARGETS, CONCEPTUAL MODELS AND THE MONITORING NETWORK DESIGN

4.1 The mine site

The main source of pollution at the mine site is metalliferous acid drainage, both from mine runoff and mine waste. By essence, it cannot be stopped: the solid sources are the sulphidic rocks and waste, exposed to weathering and oxidation. Data are provided in Table 1.

The main vector is the Kirkalon brook, as no continuous aquifer occurs in the crystalline host rocks (Fig. 2). The main mitigating process is acid neutralisation, which reduces quickly the metal contents of water. However, neutralisation causes metal precipitation, and further migration of the pollution through sediments transport (Berger et al., 2000).

The highest concentrations of metals, especially cadmium, were observed (Table 1) out of the open pit and at the bottom drainage of the waste piles.

Passive remediation can be implemented through filling a dam with crushed limestone.

4.2 The plant site

Various sources of pollution are observed at the mine site: ore stockpiles, concentrates, leftover processing chemicals, and fine-grained processing waste (tailings) stored in dams (Triantafyllidis et al., 2006).

The latter are by far the most bulky, and tend to escape to the river through dam failures. Large quantities were flushed down to the Eirini river (Fig. 3).

They show lower concentrations in metals than extraction waste (Table 2), but metals may be more bioavailable.

The main remediation actions are site cleanup for chemicals and concentrates, and tailing dams restructuration and consolidation.

4.3 Downstream the sites

The only sources of pollution in the lower catchment linked with the former mine site are local accumulations of sediments in the hydrographic network.

The main objective of monitoring (Fig. 4) will be to follow carefully the quality of pumped groundwater (drinking and agricultural purposes). Monitoring the emissions to the sea is also necessary.

5. CONCLUSIONS AND FUTURE ACTIONS

Metal pollution from the mine site runoff and mine waste is a long-term issue and must be monitored, with or without remediation. The locations proposed on Figure 1 allow to measure.

Table 2: Geochemical data, plant area.

Media	Concentrate	Tailings	Ground-water near plant	River water near plant	River Sed. Near plant	Soil near plant
Unit	wt %	mg/kg	µg/L	µg/L	mg/kg	mg/kg
Cu	1.1-2.6	295	6-20	‘6-10	354	80-240
Pb	16.5-24.4	6820	5-12	<5	556-9138	700–1200
Zn	5.6-21.6	11600	9000-200000	2200 – 5400	2642-145148	800-33000
Cd		157	100-2700	26 - 72	20.2-970	<250
pH			5.3- 6.9	7.5- 8.3		

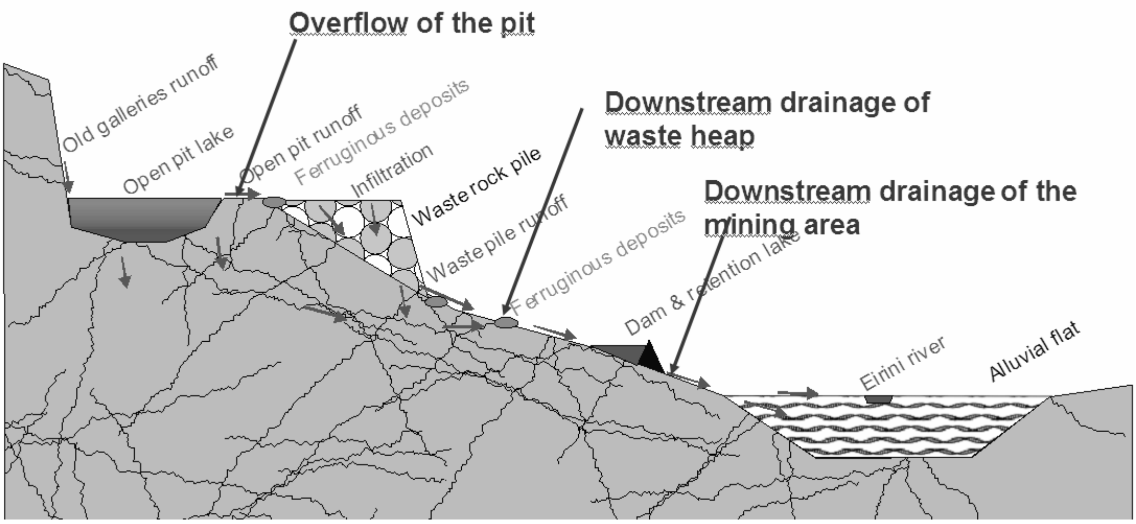

Figure 2: Location of the monitoring network points, downstream the mine site.

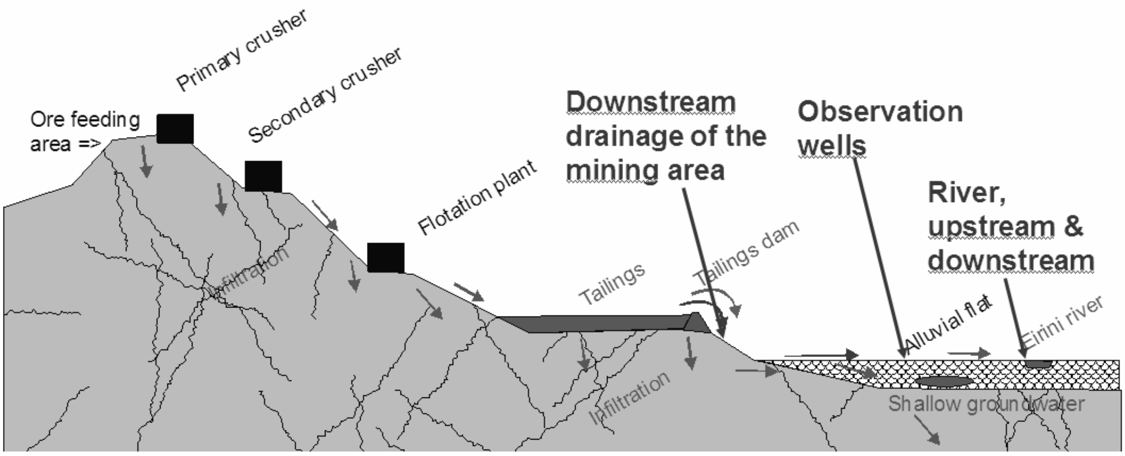

Figure 3: Location of the monitoring network points, at the plant site.

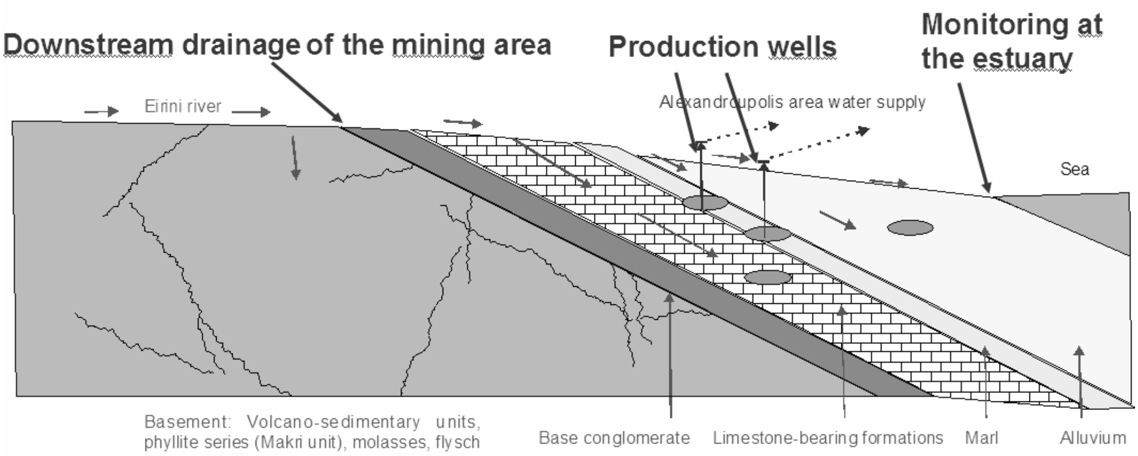

Figure 4: Location of the monitoring network points, downstream the plant site.

- the raw pollution, especially pulses in case of rainstorms, which will be the basis of any community alert system,
- the efficiency of passive remediation, below the dam.

At the former plant site, once chemicals are removed, the main issue is dam stability or refurbishment, and subsequent monitoring is required, as well as for dams stability and for drainage water chemistry.

Downstream the plant site, and near the main settlements and cultivated areas, the main objective of monitoring is to guarantee water and soil resources quality. However, estuary monitoring was proposed, as most of the pollutants emitted by the site end up in solute or solid form in the sea.

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