

## Assessment of contaminants transport in a watershed affected by acid mine drainage, by coupling hydrological and geochemical modeling tools



Nymphodora Papassiopi<sup>a</sup>, Christina Zaharia<sup>a</sup>, Anthimos Xenidis<sup>a,\*</sup>, Katerina Adam<sup>a</sup>, Alexandros Liakopoulos<sup>b</sup>, Ioannis Romaidis<sup>b</sup>

<sup>a</sup>School of Mining and Metallurgical Engineering, National Technical University of Athens, Zografos Campus, Athens GR-15780, Greece

<sup>b</sup>NCSD Institute of Geology and Mineral Exploration (IGME), Acharnai GR-13677, Greece

### ARTICLE INFO

#### Article history:

Received 14 December 2013

Accepted 5 April 2014

Available online 4 May 2014

#### Keywords:

Acid Mine Drainage (AMD)

SWAT model

PHREEQC model

Aqueous contaminants

Watershed modeling

### ABSTRACT

Erini Stream (Thrace, northeastern Greece) is adversely affected by the presence of an abandoned mixed sulfide mine located in the upper watershed. The GIS based model SWAT (Soil Water and Assessment Tool) was applied to characterize hydrologic processes in the watershed. Model performance was evaluated by comparing the simulation results with field data including flow and concentration measurements from 12 monitoring points, for the time period from June 2005 to July 2006. Flow rate results indicated good agreement between simulated and measured data, with coefficient correlations  $R^2$  in the range of 0.74–0.89. Simulation was focused on the dispersion of three pollutants, Zn, Cd and Mn. Using SWAT alone, simulation results systematically overestimated pollutants levels in Erini Stream.

Geochemical model PHREEQC was used in combination with SWAT to obtain more accurate predictions regarding contaminants concentrations along the course of Erini Stream. The profiles of main metal contaminants, i.e. Zn, Cd and Mn, under wet conditions, were described with satisfactory precision assuming equilibrium with the carbonate minerals  $\text{ZnCO}_3 \cdot \text{H}_2\text{O}$  and otavite and partial supersaturation with respect to rhodochrosite. However, precipitation of discrete carbonate phases does not seem to be the predominant attenuation mechanism under dry conditions. Coprecipitation or sorption on the surface of precipitating calcite is another potential removal mechanism under these conditions.

The methodology presented allows the reliable assessment of acid mine drainage impacts in the downstream aquatic environment and the design of effective measures for its mitigation based on an optimized number of monitoring data.

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## 1. Introduction

Erini Stream in Thrace, northeastern Greece, accepts the acid mine drainage from an abandoned Pb–Zn sulfide mine located in the mountainous northern part of the watershed (218 km<sup>2</sup>) (Fig. 1). Mineral exploration in the area for sulfide base metals and silver is reported since 1890 and sporadic exploitation of the deposit commenced in the 1930s. The most intensive exploitation, leading to the production of approximately 450,000 tons of Pb–Zn sulfide ore, took place between 1973 and 1992. This activity resulted in a long network of underground galleries, an open pit mine, widespread dumps of waste rock around the mining operations and a number of imperfectly confined tailings dams close to the flotation plant. The mining operations and the uncontrolled disposal of waste rocks cover an area of 77 ha and are located at

the watershed of Kirkalon Stream, a tributary of Erini, at 5 km north of the confluence (Fig. 1). The beneficiation plant and the nearby tailings dams occupy a surface of about 18 ha and are located on the confluence of two streams.

The sulfide minerals remaining on the walls of the underground and surface mine works, as well as in the stockpiled waste materials, are oxidized, due to their contact with atmospheric oxygen and meteoric waters, and generate acidic highly contaminated waters, a process known as Acid Mine Drainage (AMD) formation. AMD usually contains high concentrations of heavy metals, iron being the major metal contaminant and other toxic elements, as well as sulfates and proton acidity. Depending on the mineralogy of the ore, other dissolved metals usually encountered in AMD include zinc (Zn), copper (Cu), manganese (Mn), nickel (Ni) as well as cadmium (Cd) and mercury (Hg). Dissolved arsenic (As) is also reported in AMD, should arsenopyrite (FeAsS) be present in the mineralized rock. Once generated, AMD migrates away from the sources and deposits its load to the aquatic and terrestrial

\* Corresponding author. Tel.: +30 210 7722300; fax: +30 210 7722129.

E-mail address: [axen@metal.ntua.gr](mailto:axen@metal.ntua.gr) (A. Xenidis).

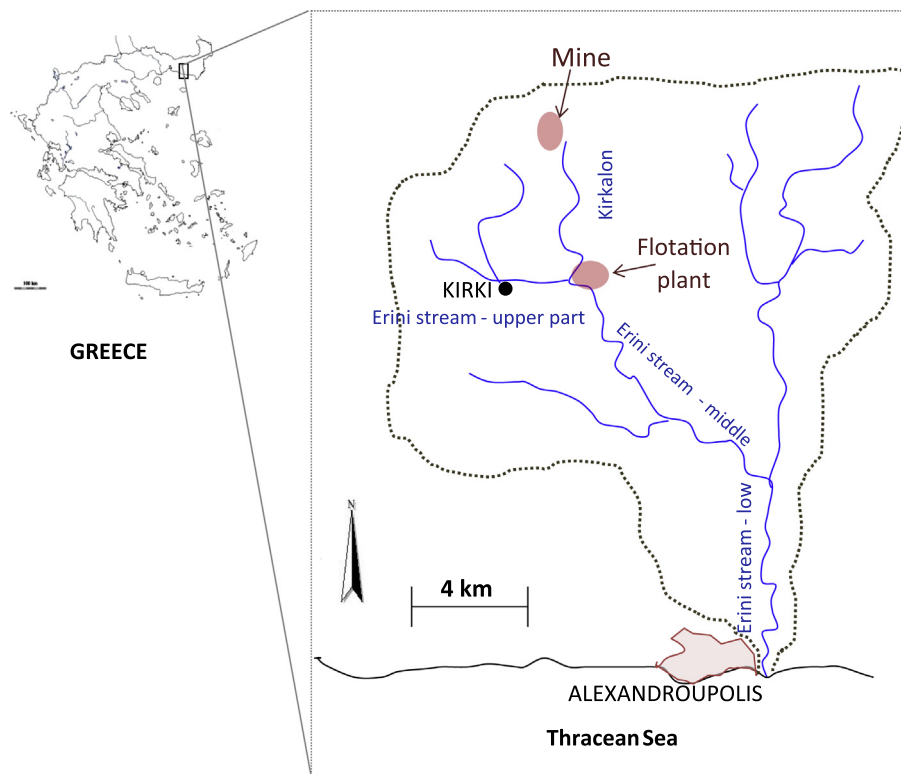


Fig. 1. Schematic view of the study area, indicating mine and flotation plant locations.

ecosystems, causing significant contamination. The problem is particularly acute in areas with historic mining activities where abandoned mines are found. In order to assess AMD migration and potential impacts on the downstream environment, hydrometric and water quality monitoring installations are required, ideally supported by mathematical modeling (ERMITE, 2004).

Several studies were carried out since 2000 for the environmental characterization of Kirki's abandoned mining site, as well as for the evaluation of its impact on the quality of nearby natural receivers, i.e. surface and ground waters, soils and sediments (Triantafyllidis and Scarpelis, 2006; Triantafyllidis et al., 2007; Arikas et al., 2007; Michael and Dimadis, 2006; Romaidis, 2007; Liakopoulos, 2009; Papassiopi et al., 2009; Liakopoulos et al. 2010; Loupasakis and Konstantopoulou, 2010).

Within the framework of assessing the impacts of AMD phenomenon in the area, the present paper examines the potential applicability of the hydrological model SWAT (Soil and Water Assessment Tool), in combination with the geochemical model PHREEQC, as a tool for predicting the quality and quantity of surface waters in this medium size catchment area affected by the AMD phenomenon.

SWAT is a basin scale, physically based, distributed model, which simulates the rainfall-runoff process, sediment transport and pollutant-nutrient loads in large watersheds (Gassman et al., 2007). It was developed by the US Department of Agriculture (USDA) in the early 1990s and has been extensively used internationally for assessing water resource and pollution problems and alternative water management scenarios. Many of the SWAT applications were driven by the needs of various governmental agencies, particularly in the US and the European Union, to assess anthropogenic, climate change and other influences on a wide range of water resources. The model has been also applied to describe hydrological and water management problems in several watersheds in Greece (Varanou et al., 2002; Gikas et al., 2006; Pisinaras et al., 2010).

Pollution problems addressed using SWAT are mainly related with agricultural practices and concern high levels of N, P, organic carbon compounds, and pesticides. Amongst the wide range of relevant publications, there was only one paper where SWAT was applied for the estimation of pollutants transfer in the case of AMD affected areas, the Meca River basin in SW Spain (Galvan et al., 2009).

Despite the need for modeling AMD migration in abandoned mine lands, there are very few models specifically developed to describe the transport of contaminants in AMD affected surface waters. An example is the OTEQ model (Runkel, 1998, 2010; Runkel and Kimball, 2002), a reactive transport model for flow in streams incorporating geochemical equilibrium calculations. The model does not include hydrologic calculations taking into account the characteristics of the watershed, and thus the stream flow rates are not calculated by the model but are introduced as input data.

Another widely used model, which couples the geochemical modeling with one-dimensional transport principles, is PHREEQC (Parkhurst and Appelo, 1999; Charlton and Parkhurst, 2011). PHREEQC constitutes a geochemical reaction model that simulates a variety of geochemical processes including equilibrium between water and minerals, ion exchangers, surface complexes, solid solutions, and gases. PHREEQC presents capabilities for 1D reactive-transport model, including such processes as multicomponent diffusion and advection of aqueous species, as well as dispersive and advective transport of surface-complexing species. PHREEQC has been often used as a geochemical calculation module in reactive-transport models. Webb and Linnard (2006) combined PHREEQC with a topography-based hydrological model (TOPMODEL), but there are limited published data regarding the capabilities and the application fields of the combined model.

## 2. Study area description

Erini Stream watershed is located in Thrace, NE Greece, north of Alexandroupolis city. Geologically the watershed belongs to

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