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Assessment of soil contamination around an abandoned mine in a semi-arid environment using geochemistry and geostatistics: Pre-work of geochemical process modeling with numerical models

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ABSTRACT

One of the most serious environmental issues related to mining industry in Morocco and elsewhere around the world, is the pollution from abandoned mine sites. Mine wastes cause obvious sources of soil contaminations. Climatic effects such as heavy rainfall engender metal dispersion in semi-arid areas, since soils are typically and scarcely vegetated. In this study, extension and magnitude of soil contaminations with toxic elements from abandoned Kettara mine, in Morocco, are assessed using geochemical analysis and geostatistics for mapping. Soils and mine wastes are sampled and analyzed for 41 chemical elements (Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, Al, Na, K, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, Li, S, Rb and Hf). Based on enrichment factor (EF), only five elements of interest (Cu, Pb, Zn, As, and Fe) were selected in this research. Geochemical background is determined with exploratory data analysis and geochemical maps were elaborated using geostatistics in Geographic Information System (GIS) environment.

The obtained results show that Kettara soils are contaminated with metals and metalloid that exceed the established geochemical background values (Cu≈43.8 mg/kg, Pb≈21.8 mg/kg, Zn≈102.6 mg/kg, As≈13.9 mg/kg and Fe≈56,978 mg/kg). Geochemical maps show that the deposited mine wastes are responsible for soil contaminations with released metals and metalloid that have been dispersed downstream from the mine waste mainly, through water after rainfall. For sustainable development and environmental planning, the current study is expected to serve as a reference for politicians, managers, and decision makers to assess soil contaminations in abandoned mine sites in Morocco.

1. Introduction

Acid Mine Drainage (AMD) from mine waste and contaminations of soils and water with metals are considered as major environment problems in mining areas (U.S. Bureau of Mines, 1994). This environment phenomenon is produced with oxidation of sulfide minerals e.g. pyrite and pyrrhotite (Bussiere, 2009; Hakkou et al., 2008a). Consequently, acidification would increase the dissolution of toxic metals from tailings, waste rock piles, and open pits. Therefore, soil and water ecosystem will be contaminated (Bell and Donnelly, 2006; Sams and Beer, 2000). Certainly, as rainfall water infiltrates into the underground soil/rock, it can cause pore-water flow in the pore space of the soil/rock. The resulting pore-water flow can be advective or convective (Zhao et al., 2004, 2008a) depending on geological conditions of the mine site. When the pore-water becomes in contact with the soil/rock, it can react chemically with the mine waste dissolving heavy metals at the mine site. Since the dissolved heavy metals can be transported in the soil/rock through pore-water advection, convection and solute diffusion/dispersion (Zhao et al., 2007), they can contaminate both the land and the groundwater at the mine site. In addition, as demonstrated theoretically, the dissolved metal front may become unstable when it propagates in the soil/rock at the mine site (Zhao et al., 2008b, 2010a). This is the scientific problem, known as the mine site contamination, which is the focus of this study.

With the stimulus of exploring giant ore deposits in the deep earth, extensive and systematic work has been conducted to develop advanced computational methods and algorithms for simulating physical and chemical processes associated with ore body formation and mineralization within the Earth's crust (Zhao et al., 2009, 2010b). As a result, a new emerging discipline, known as the computational geosciences (Zhao et al., 2009), has been established. Due to mathematical similarity, the advanced computational methods and algorithms (Zhao et al.,

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2006, 2009) can be also used to solve mine site contamination problems if the geological and the geochemical data are available at the mine site. From this point of view, the scientific significance of this study can be described as follows. First, detailed geochemical data produced in this study can be used as an example to extend the advanced computational methods and algorithms to the computational simulation of mine site contamination problems. This will answer how and why the mine site is contaminated in a scientific manner. Second, advanced computational methods and algorithms are then used to develop techniques to remove heavy metals from the contaminated mine site, which is known as the mine site remediation problem (Zhao et al., 2012) and has great practical significance in the current world.

Furthermore, knowledge of soil geochemistry is fundamental when we attempt to determine the effects stemming from an anthropogenic activity and its impact on the geo-ecosystems as a result of its toxicities (Albanese et al., 2007; Cicchella et al., 2005; Giaccio et al., 2012; Guillén et al., 2011, 2012). In this respect, it is essential to establish geochemical maps for chemical elements associated with different lithologies in order to distinguish if their source is geogenic or anthropogenic (Plant et al., 2001). In addition of the scientific or mining standpoint, geochemical maps constitute an effective tool for environmental planning (Ferguson and Kasamas, 1999; Li et al., 2004). They reveal information about source, distribution, and dynamics of chemical elements. Geochemical maps include both the geogenic concentration or geochemical background (GB) value, and the concentration that is the result of anthropogenic activity (Guillén et al., 2011). This explains why GB defined by Hawkes and Webb (1962) as "*the normal abundance of a chemical element in barren earth material*" has become crucial in environmental studies. It was introduced to differentiate between normal and abnormal element concentration (Martínez et al., 2007). Exploratory Data Analysis (EDA) has been recommended as an effective tool to determine the GB (Zhou and Xia, 2010). According to the literature, this method was tested and proved by numerous authors (Bounessah and Atkin, 2003; Reimann et al., 2005).

Finally, GIS based on geostatistical analysis is one of the most important tools for studying environmental geochemistry problems (Acosta et al., 2011). It provides an effective means for researching the spatial variability of pollutants (Sun et al., 2012). Geostatistics is an advanced methodology that facilitates quantification of the spatial features of soil parameters and enables spatial interpolation (Carlon et al., 2001; Zhang et al., 2000). According to the literature, numerous authors have used kriging analysis in GIS environment to elaborate geochemical maps to quantify both extension and magnitude of contamination with toxic elements (García-Lorenzo et al., 2012; Li and Feng, 2012; Li et al., 2004; Nakayama et al., 2011).

The abandoned Kettara mine site (Morocco) was selected to analyze the impact of mining activity on the surrounding soils. The objectives of this study were as follows: 1) geochemical characterization of Kettara soils and tailings; 2) determination of GB values of selected chemical elements in Kettara soils; and 3) elaboration of geochemical maps regarding the selected toxic elements and their comparison with the elaborated GB to reveal the degree of pollution of the Kettara mine site surrounding soils and to examine possible health risks.

2. Materials and methods

2.1. Study site

The abandoned Kettara mine is located approximately 35 km northwest of Marrakech city in the core of the central Jebilet Mountains (Fig. 1). According to the latest governmental census (2004), the population of Kettara village is approximately 2000 people. The climate of this region is classified as semi-arid environment with average maximum and minimum temperature ranging from 12 °C in January to 29 °C in July, respectively. The average annual rainfall is 250 mm. The potential evapotranspiration rate surpasses 2500 mm/year. NE–SW wind flow is prevailing in the study site (ONEM, 1997). Perennial streams do not exist and surface water consists of ephemeral watercourses that are operational only during rainfall events.

The Kettara mine had undergone three mine exploitation phases. In the first phase, between 1938 and 1962, the iron oxide was extracted from the iron hat "gossans" to produce red oxide (50 to 58% of Fe) for paint industry. In the second phase, between 1955 and 1966, the zone of cementation was exploited for pyrite (180,000 t with 38 wt.% of sulfide) (Huvelin, 1977). During these two phases the ores were delivered in their raw state without any mineralogical concentration, and the mine wastes were about 1 million ton (Mt) of coarse waste rocks. In the third and final phase, between 1964 and 1981, the mine produced more than 5.2 Mt of pyrrhotite concentrate containing an average of 29 wt.% sulfide. The pyrrhotite was extracted from the ore by gravimetric separation (jigs). This ore enrichment process generated a wide range of particle size fractions in the mine wastes (jigs refuse materials). These latter can be divided into two broad classes of materials: coarse mine wastes (fine gravel) and fine mine wastes (silt). Throughout this period, more than 3 Mt of mine wastes were stockpiled over an area of about 30 ha (Fig. 2). The Kettara wastes contain 1.6 to 14.5 wt.% sulfur, mainly sulfide minerals (e.g., pyrrhotite, pyrite, chalcopyrite, galena, and sphalerite) (Hakkou et al., 2008a). The Kettara mine wastes have produced significant amounts of AMD. Previous researches (Hakkou et al., 2008b) have shown that effluent water samples had low pH (2.9 to 4.2), and high concentrations of sulfate (from 47 to 5000 mg/L) and iron (from 1 to 1200 mg/L). Furthermore, the Cu and Zn concentrations had reached 58 and 45 mg/L, respectively. At the Kettara mine site, several secondary minerals have been observed at the surface (e.g., goethite, jarosite, alunite, gypsum). The presence of these minerals in large quantities shows that AMD generation is very active at Kettara (Hakkou et al., 2008a).

The Kettara sulfide deposit is a typical example of metamorphosed deposits hosted by Visean volcano-sedimentary formations. The mineralized body consists of major and minor lenses of massive pyrrhotite, with small amounts of sphalerite, galena, chalcopyrite, pyrite, arsenopyrite and glaucodot. The structure resulted from an intra-Westphalian tectono-metamorphic phase of the Hercynian orogeny (Hibti et al., 1999). The substrate of Kettara is composed of fractured and altered shale, which facilitates AMD infiltration. Furthermore, the principal groundwater table is located in this formation and has a depth of between 10 m and 20 m. According to Lghoul et al. (2012), groundwater sampled at Kettara mine site from wells located downstream of the mine wastes is contaminated by the AMD, mainly by sulfates ($>$1200 mg/L) and presents high conductivity values, 3000 to 3680 μS/cm.

2.2. Sampling and samples preparation

Special consideration was given to the used criteria to select sampling points' locations. After a review of topographic and geologic maps, and according to previous studies on the abandoned Kettara mine (Hakkou et al., 2008a; Khalil et al., 2011), soil sampling was established in 3 different areas based on the location of the mine wastes. The sampling design was made to compare concentration gradient and possible chemical element mobilization. The distance between sampling points varies from 150 to 350 m. Four groups of soil samples have been collected: 1) samples located upstream of the mine waste (13 samples); 2) samples located nearby the mine waste (27 samples); 3) samples located downstream of the mine site (22 samples); and 4) mine waste samples from the Kettara mine tailings (12 samples). Finally, 62 soil samples (from S1 to S62) and 12 mine waste samples (from R1 to R12) were collected within the study site, approximately 6 km^2 (Fig. 2). Geographic coordinates of sampling points were measured using a Global Positioning System (GPS) within $\pm$5 m accuracy, with the "Lambert North Morocco" map projection.