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Assessment and mobility of heavy metals in carbonated soils contaminated by old mine tailings in North Tunisia

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ABSTRACT

The activity of the former Pb–Zn mine of Jebel Ghozlane, located in the extreme north of Tunisia, generated during the last century large quantities of tailings (extraction, flotation, gravimetry), which are deposited without concern for environmental issues. The tailings contain both primary (galena, sphalerite, pyrite) and secondary (cerussite, smithsonite, iron oxi-hydroxides) heavy metals bearing minerals. The gangue minerals are composed of calcite, dolomite, barite, celestite and quartz. The concentrations of Pb, Zn and Cd in the tailings vary from 1.2% to 5.7%, 9.3% to 13.6%, and 185.6 to 410.6 mg kg^{-1}, respectively. The soils surrounding the tailings piles, developed on a calcareous bedrock, are characterized by alkaline pH (H_2O) ranging from 6.8 to 7.9. In addition, cation-exchange capacity (CEC) was low with a mean value of 4.25 cmol kg^{-1} and organic matter (OM) content varied between 2.23% and 6.13%. These soils contain high amounts of Pb, Zn and Cd, that can reach 3052 mg kg^{-1}, 22,086 mg kg^{-1} and 99.3 mg kg^{-1}, respectively. The contamination levels by heavy metals (HM) in the soils were evaluated using the modified degree of contamination (mC_d). This evaluation shows that 60% of the analyzed soils are between the high degree and the ultra-high degree of contamination classes. The extraction tests using deionised water, salt ($CaCl_2$), low-molecular-weight organic acids (LMWOAs) and chelating agent (DTPA) solutions were performed to evaluate the mobility of Pb, Zn and Cd in soil samples. Results show that, the extractability of heavy metals is slightly influenced by pH, CEC and total carbonate (TC) content of the soil. The amounts extracted with water and $CaCl_2$ are negligible. The highest percentages of total heavy metals are extracted with DTPA (0.7–19.5% for Pb, 0.3–6.2% for Zn and 0.4–11.9% for Cd) and at a lesser degree by LMWOAs (0.1–0.8% for Pb, 0.1–2.5% for Zn and 0.1–1.9% for Cd). These results showed that the mobility of metals is generally very low and influenced by the high carbonate content of soils.

1. Introduction

Contamination of soils by heavy metals is one of the main environmental problems that affect both human health and ecosystems (Kabata-Pendias, 2004; Clemente et al., 2007; Wang et al., 2008). In environmental studies, the total concentration of heavy metals includes mobile forms which are easily exchangeable ions and non-mobile forms that are more strongly fixed to the solid phase of the soil (Gupta and Sinha, 2006). In case of plants, metals present as free ions in the soil solution may be more toxic than metals in the complexed state (Gupta and Sinha, 2006). According to Kabata-Pendias (1993), the determination of total metal content in the soil allows to assess the potential risk of pollution; however, only the labile metal species (soluble, exchangeable and chelated) are available to plants. Thus, the determination of total concentrations should be complemented by assessing available fractions of metals (Buccolieri et al., 2009). Many different parameters rule the mobility of heavy metals in soils, notably pH, organic matter (OM) and cation exchange capacity (CEC) (Alloway, 1990; Pagotto, 1999; Hlavackova, 2005; Galvez-Cloutier and Lefrançois, 2005; Gupta and Sinha, 2006; Ettler et al., 2007). Several million tons of Pb–Zn ore-processing wastes were generated in northern Tunisia during the last century, and then abandoned as tailings piles in several localities, without concern for environmental issues (Souissi et al., 2013). The abandoned mine site of Jebel Ghozlane contains large amounts of tailings were left both on the watershed of the local watercourse and within farmlands. This leads to a potential risk of remobilization of metals from the soils and

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diffusion to animals and humans. Nevertheless, there is no data available on the impact of mining activities on the soils of Jebel Ghozlane site. Based on mineralogical and geochemical aspects, the purpose of this study is to afford the mineralogy and geochemistry of the tailings of Jebel Ghozlane, as well as the study of the distribution and the mobilization of heavy metals in the surrounding soils. Therefore, to establish relationships between heavy metals and soil properties (pH, OM, CEC, TC), four simple extraction techniques were applied using H_2O, $CaCl_2$, diethylenetriaminepentaacetic acid (DTPA) and a mixture of low molecular-weight organic acids (LMWOAs) on soil samples that contain high concentrations of metals.

2. Presentation of the study area

Jebel Ghozlane is located (Fig. 1) near the Mediterranean coastline, 80 km to the north of Tunis City. The geology of the Bechateur district was discussed by Melki et al. (2001) and Jemmali et al. (2011b). The stratigraphy of this district consists mainly of Triassic and Upper Cretaceous to Eocene rocks (Fig. 1). The Triassic rocks are made of a composite breccia including variegated clays (illite, kaolinite, chlorite), sandstones, dolostones, and altered basalts. The Upper Cretaceous to Paleocene rocks consist of marl-limestone alternations. The Lower Eocene rocks are composed of pelagic limestones. This series is overlain by Upper Eocene marls. The lithologies are represented by marine deposits.

The ore minerals consist of galena, sphalerite, barite and celestite accompanied with minor pyrite occurring as open space fillings within dolomitic rocks (Jemmali et al., 2013) along the Triassic/Eocene boundary. At the closure of the mine in the early 1950's, the total production was about 6680 tons of Pb and 53,000 tons of Zn (Cherif Ben Hassene, 2006). The Jebel Ghozlane anticline trends in the NE–SW (Atlasic) direction, and is characterized by low-reliefs and a subhumid climate with dry and warm summer seasons and relatively wet winters (TPE, 2010). The prevailing wind direction is from West-North-West (INM, 2009). The study area receives more than 650 mm mean rainfall per year (INM, 2009) and is characterized by a reduced hydrographic network made by Wadi Bou Rakrouk and Wadi Ladhbaa, that flow only during rainy seasons. Wadi Bou Rakrouk is the most important water course, which drains the largest tailing's pile DI and discharges into the sea (Fig. 2). The soil of the mining district is of rendzine type, developed on a calcareous rock material (Tunisian Ministry of Agriculture, 1973). A small village is located at about 2 km from the mine. Agricultural activities (*Hordeum vulgare)* are well developed east of the mining site, while spontaneous vegetation (e.g.: *Hypericum triquetrifolium*, *Chrysanthemum coronarium*, *Sisymbrium officinale*) is also quite abundant.

3. Material and methods

3.1. Sampling

The tailings are stored in three piles (Fig. 2): DI, corresponds to the large flotation-tailings pile; DII, makes the small flotation-tailings pile; and DIII, which is the oldest pile, is made of gravimetry tailings. Two kilograms of material were collected along a vertical profile from base to top of each of the tailings piles (Fig. 3). In total, 18 samples were collected: 12 samples from DI, 4 samples from DII and 2 samples from DIII. Each sample was stored in a clean polyethylene bag. In the lab, all samples were dried (50 °C for 48 h) and then quartered. One representative sample was prepared for each tailings pile, by mixing the individual quarters of all samples from the corresponding pile; and then each of them was screened for the fraction below 2 mm. Grain size

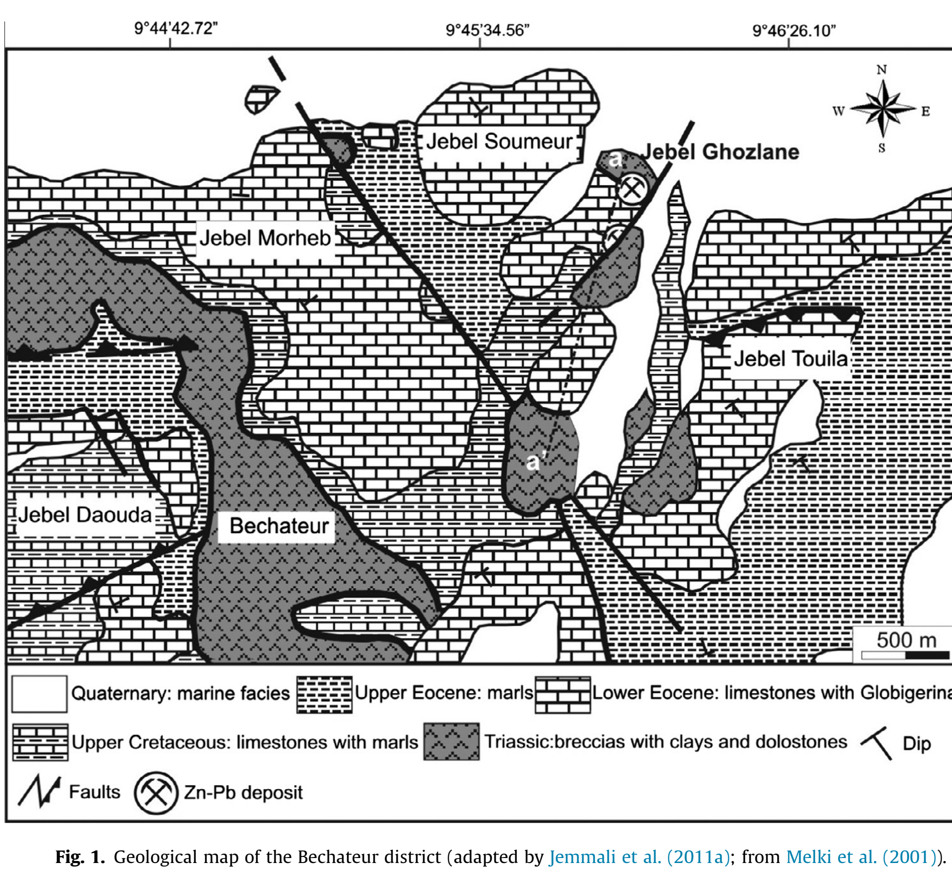

Fig. 1. Geological map of the Bechateur district (adapted by Jemmali et al. (2011a); from Melki et al. (2001)).