Are abandoned mine tailings of Northern Tunisia a source of metal contamination in surface water?

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Abstract This study addresses to possible contamination of surface water with metals (Pb, Zn, Cd) transferred by hydric erosion from abandoned mine tailings in North Tunisia. Jebel Ressas is taken as a representative example of North Tunisian mining activity in carbonate geological context and semi-arid climate. On the basis of precise mineralogical and chemical characterizations of the tailings, thermodynamic modeling of their meteoric alteration permits to calculate maximum metals concentrations in surface water controlled by metal-bearing phases solubility. Increasing salinity in surface water due to evaporation is considered and has no significant impact on metal contamination due to carbonate environment buffering.

Key Words Jebel Ressas, Pb, Zn, Cd, thermodynamical modelling, salinity.

Introduction

Tunisia has a well established metal ore extraction traditional industry dating from more than two thousand years. From pre-Roman period, huge quantities of metals have been extracted particularly since the end of the 19th century when large-scale mining operations started (Sainfeld, 1952). The whole national metal production has been estimated at 55 MT of iron, 2.3 MT of lead and 2 MT of zinc (O.N.M., 2010). Now that mining activity stopped (O.N.M., 2010), tailings and mining dumps remain abandoned without any specific management. In mineralized areas of Northern Tunisia (fig.1), tailings contain high proportions of Pb and Zn carbonates and sulphides which are exposed to mechanical and chemical erosion by heavy rainfall events and/or to eolian erosion due to semi-arid Mediterranean climatic conditions (Mlayah and al., 2009, Boussen and al., 2010). Owing to these processes, contamination of surface water by metallic cations is possible and must be considered to better manage these sites.
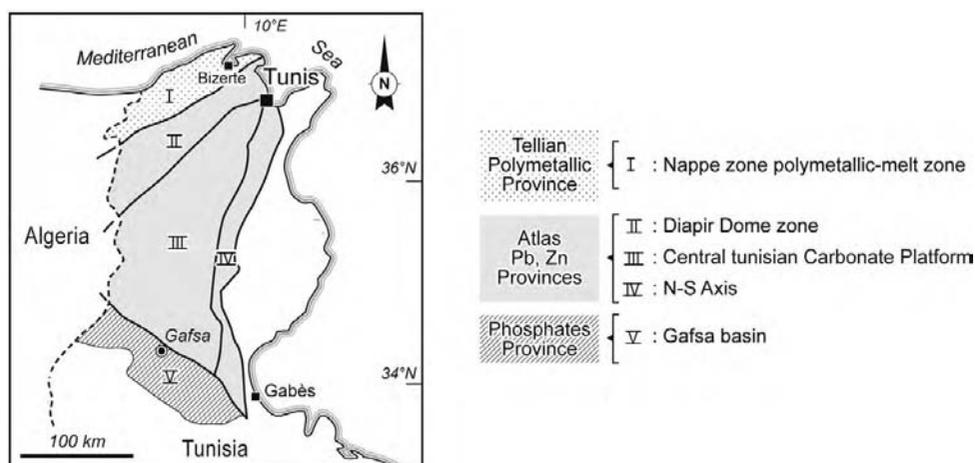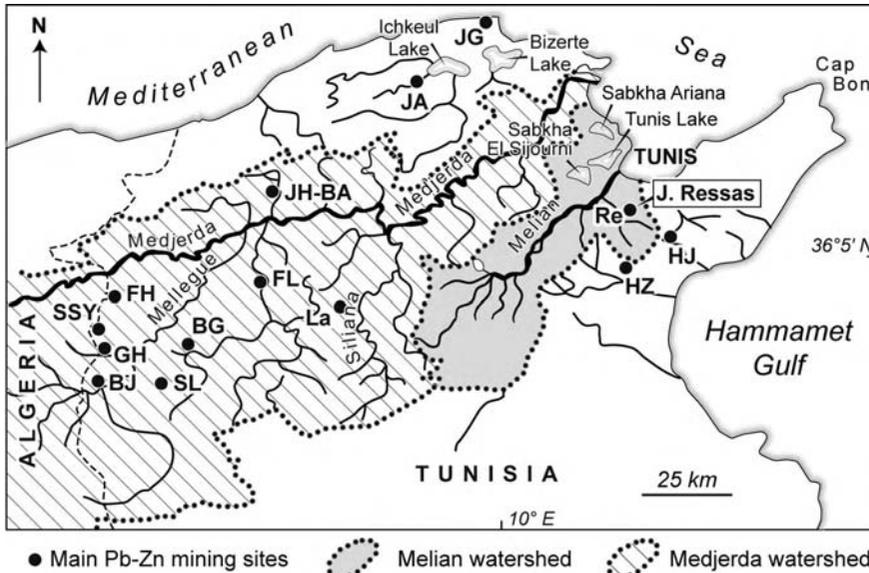

Figure 1 Metallogenic provinces of Tunisia

Figure 2 Main draining network of northern Tunisia with most important Pb, Zn abandoned mining sites (BA: Sidi Bouaouane; BG: Bougrine;BJ: Boujabeur; FH: Fej Hsnine; FL: Fej Lahdoum; GH: Guern Halfay; HJ: Hamman Jedidi; HZ: Hamman Zriba; JA: Jalt; JB: Jebel Hallouf; JG: Jebel Gozlane;La: Lakhouat; RE: Jebel Ressas; SL: Slata; SSY: Sakiet Sidi Youssef)

In Northern Tunisia, the main draining surface water network consists of Medjerda and Melian rivers and tributaries and continental lakes, coastal lagoons, sabkhas and reservoir dams (fig. 2). During the dry period, salinity of surface water sensibly increases from $1\,g{\cdot}L^{-1}$ to $2\,g{\cdot}L^{-1}$ in the Medjerda river (Rahaingomanana, 1998), up to $50\,g{\cdot}L^{-1}$ in the Ichkeul lake (Casagranda et al., 2007) and up to $65\,g{\cdot}L^{-1}$ in the Ghor el Melh coastal lagoon (Thomson et al., 2009).

The present study addresses the possible surface water contamination due to metal bearing tailings of the numerous Pb-Zn abandoned mining sites located in the watersheds (Fig. 2). Metal contents in percolating water after rainfall events were calculated taking into account the regional carbonated context and different salinity conditions due to occurrence of salt outcrops, to evaporation or mixture with various surface water.

Materials and Methods

Modeling was based on the mineralogical and chemical characterization of Jebel Ressas tailings. The abandoned mining and milling site of Jebel Ressas is located 30 km Southeast of Tunis and connected to a tributary of Melian River which is the second permanent river of North Tunisia (fig.2). Its Pb-Zn mining activity resulted in two millions of tons of gravimetry and flotation wastes with a weak cohesion and fine grain size less than 80.1 μm. No vegetation has grown on the dumps and no specific management was conceived to prevent their erosion and chemical alteration. Tailings contain $4.66_{0.98}Zn_{0.2}As_{0.01}S_{1.99}$ and galena PbS), as silicate (hemimorphite $Zn_4Si_2O_7H_2O$) and carbonates (smithsonite $ZnCO_3$, hydrozincite $Zn_5(OH)_6(CO_3)_2$ and cerussite $PbCO_3$) (Ghorbel et al., 2010). Cd is associated to Zn in sphalerite and smithsonite up to ≈ 0.5 wt %. Iron oxy-hydroxides display minor contents of Pb and Zn. Calcite is the major mineral in the tailings and quartz and alumino-silicates were also observed in smaller proportions. These mineral assemblages are representative of those encountered in other Pb, Zn sites of northern Tunisia (Boussen et al., 2010).

Geochemical modeling was performed at 25 °C with Phreeqc geochemical package (Parkhust and Appelo, 1999) using llnl.dat database implemented with the dissolution constant of hemimorphite (McPhail et al., 2006). A first step consisted in simulating the circulation of rain in the tailings and its interaction with the observed minerals. Thermodynamic equilibrium between

Table 1 Results of geochemical modeling for each step of the simulation

Step	pH	Ionic strength	[Pb]$_{total}$		[Zn]$_{total}$	
		(mol L^{-1})	(mol L^{-1})	(µg L^{-1})	(mol L^{-1})	(µg L^{-1})
draining water	9.8	0.004	5.2 10^{-7}	108	6.7 10^{-10}	0.044
30% evaporation	9.7	0.005	4.1 10^{-7}	85	5.5 10^{-10}	0.036
60% evaporation	9.6	0.005	3.6 10^{-7}	75	5.3 10^{-10}	0.035
2g L^{-1} salinity	9.8	0.14	5.1 10^{-7}	106	1.3 10^{-9}	0.085
65g L^{-1} salinity	9.9	1.03	8.2 10^{-7}	170	4.2 10^{-9}	0.275

the circulating fluid and oxidized metal bearing phases in that carbonated context controls maximum aqueous metal concentrations. In a second step two rates of evaporation of 30% and 60% were considered for the resulting draining water. Finally, the effect of an increase of salinity up to 2 and 65 g·L^{-1}, is simulated by increasing the NaCl concentration in the fluid. For each step, equilibrium with calcite and quartz are imposed to account for the carbonate environment context and to control the silica concentration in equilibrium with hemimorphite.

Results

Values of pH, ionic strength and aqueous total Pb and Zn concentrations for the different steps of modeling are provided in table 1. The high values of pH reflect the buffering effect of calcite. When sulphides dissolve in the percolating rain the produced acidity is neutralized by calcite dissolution and the resulting high content of carbonate anions tend to buffer the pH up to 9.9. The relative low values of the ionic strength in the draining water and the evaporated fluids are also controlled by the carbonate content. On the contrary, high ionic strength of the saline water depends essentially on NaCl concentration. Total Pb and Zn concentrations are controlled by cerussite and hemimorphite equilibrium, respectively. Geochemical modeling does not favour other Zn bearing phases like smithsonite, hydrozincite and willemite which have been observed in the tailings.

The chemical composition of the draining water does not change significantly with evaporation since equilibrium between the solutions and the mineral phases remain the same. Cerussite and hemimorphite control Pb and Zn concentrations and precipitate whatever the evaporation rate is. Calcite controls both calcium and carbonate concentrations which are the main contributors of ionic strength. Consequently, the ionic strength remains constant even when evaporation occurs. Increasing salinity to the higher value of 65 g L^{-1} leads to an increase in Pb and Zn concentrations by a factor of 2 and 7, respectively. In these solutions, metal concentrations are still controlled by cerussite and hemimorphite precipitation. However, increasing ionic strength up to 1.03 mol L^{-1} reduces by a factor of 5 the activity coefficients of Pb, Zn and carbonate aqueous species and as a result, higher concentrations are needed to reach the ionic activity product corresponding to equilibrium with these solid phases.

Discussion

Geochemical modeling of both draining water and saline surface water predicts very low concentrations of Zn and maximum Pb concentrations one order of magnitude higher than the value of 10µg L^{-1} recommended by the World Health Organization (1993). These results are based on the thermodynamic equilibrium with observed secondary mineral phases and do not take into account any kinetics. Pb and Zn concentrations are controlled by the mineralogy of secondary phases allowed to precipitate in the modeling and may change with the nature of these solid phases. For example hydrocerussite is thermodynamically more stable than cerussite but was not allowed to precipitate because not observed. If hydrocerussite could precipitate the aqueous Pb concentration would be lower by a factor of five and closer to WHO's recommended concentration. Furthermore, hydrozincite was observed in the tailings and if, for kinetic reasons, the precipitation of this phase is promoted instead of that of hemimorphite, aqueous Zn concentration should be higher by three orders of magnitude, reaching 200 µg L^{-1} in highly saline surface water. However, this value still remains lower than the WHO's recommended Zn concentration of 5000 L^{-1} (WHO, 1993).

Cd has always been analysed associated with Zn either in sphalerite or in smithsonite. Evaluation of the maximum Cd concentration controlled by equilibrium with secondary mineral phases could not be done since saturation with smithsonite is never reached in the model. Nevertheless, if the weight proportion of Cd in the tailings is estimated to 0.4% (0.02wt%/4.66wt%) and assuming that both Cd and Zn behave in the same manner, aqueous Cd concentrations may reach $10^{-3}\mu g\ L^{-1}$ or $0.8\mu g\ L^{-1}$ in high saline surface water depending on hemimorphite or smithsonite control, respectively.

Conclusions

The geochemical modeling of the draining water of abandoned Pb-Zn mining sites lead to relatively low concentrations of Zn and a Pb content one order of magnitude higher than WHO's recommended value. These aqueous metal concentrations are controlled by the precipitation of oxidized metal bearing phases. The chemistry of the studied solutions is mainly controlled by the carbonate context which prevents from water acidity and higher metal concentrations. The effect of higher salinities on metal contents is an increase of Pb and Zn concentrations by a factor 2 and 7, respectively. The metal concentrations still remain at a low level compared to those found in AMD.

As a consequence, the water quality of Medjerda and Melian rivers, lakes or coastal lagoons might be slightly impacted by metal contamination due to chemical erosion of mine tailings in this Mediterranean semi-arid context. Metal transfer through surface water network in Northern Tunisia does not appear as the main contamination transfer process. Nevertheless, supplementary field data on the chemical composition of the percolating solutions are essential in order to identify the secondary minerals which control the metal contents and to better constrain the simulation of the ultimate fate of these contaminants.

Acknowledgements

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