

Polymetallic pollution from abandoned mines in Mediterranean regions: a multidisciplinary approach to environmental risks

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Abstract Abandoned mines are a recurrent problem for nearby communities in Mediterranean regions because mine tailings represent a major source of polymetallic contamination. Metal contaminants are emitted in mining areas and dispersed by wind and water erosion in the surroundings. The goal of this literature review was to identify the specific features of polymetallic contamination arising from abandoned mines in the Mediterranean regions. Mediterranean climate conditions and local geochemical context are the most important factors that control the

metal-bearing particle dispersion toward the different compartments of ecosystems. Acid mine drainage, as an important source of damage to the environment, is limited to a certain extent by the predominance of carbonate rocks in the Mediterranean regions. In opposite, aeolian contamination is specific to the semiarid conditions of the Mediterranean climate. In this context, impacts on different compartments such as agricultural soils and edible plants or human populations were underlined. The analysis of environmental laws and regulations of North and South Mediterranean countries shows that one of the main differences is the lack of identification and definition of mining waste as a public concern in the latter countries. In order to limit the transfer of contaminants from mining waste to the different components of the environment, phytostabilization of mine tailings was considered as the more adapted green technology even in the Mediterranean region where water access is limited. Finally, this review of polymetallic pollution from abandoned mines in Mediterranean regions enabled to identify priority actions for future research.

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Introduction

The Mediterranean basin has been identified as the area most exposed to climatic and anthropogenic changes in the world (Milano et al. 2012). Among the many anthropogenic disturbances particularly traffic, industrial activities, energy production, and past and present mining activities have played a significant role in degrading the

environment of the Mediterranean region. Abandoned mining sites are of particular concern in this context, but are also good locations to investigate the impacts of metallic contaminants on the environment and on human health.

Understanding the complexity of Mediterranean mining environments, from the source of contamination to the public health concerns, requires a multidisciplinary approach. The goal of this literature review was to identify the specific features of polymetallic contamination in the Mediterranean regions with the aim of defining an integrated approach to (i) assess the associated risks, (ii) identify priority research areas, (iii) identify the constraints and approaches needed to deal with this kind of contamination, and (iv) underline differences in mining waste management in Northern and Southern Mediterranean regions.

Polymetallic ores for the production of Ag, Au, Cu, Fe, and Pb have been heavily worked in Mediterranean regions since pre-Roman times. Mn, Sb, Sn, W, and Zn have also been extensively mined since the beginning of the industrial revolution in the early nineteenth century. The extraction and concentration of metals resulted in on-site dumping of large amounts of mine wastes with high concentrations of residual metals. In addition to the extracted elements, whose toxicity is usually known, other hazardous elements such as Cd and As occur within ore paragenesis and remain in tailing dumps.

The Mediterranean climate is characterized by mild winters, hot dry summers, and rare but intense rainfall events that cause flash floods. Consequently, the hydrologic regime of Mediterranean catchments follows a very irregular seasonal pattern characterized by high runoff volumes due to the storm events and low bedrock infiltration rates (Guittonny-Philippe et al. 2014). The region is also characterized by differences in environmental standards and policies, by socioeconomic inequalities, and by political instability, particularly along the southern rim, which can influence scientific, social, and political responses to mining waste issues.

Abandoned mine sites are a recurrent issue for local populations in Mediterranean regions. These “hot spots” are usually located adjacent to villages and are surrounded by farmland. The local population is subjected to exposure to heavy metals given the characteristics of Mediterranean climate, which enhances the spread of metal contamination in the air, water, and soil. Acid mine drainage (AMD) is a major source of damage to the environment under temperate climates. However, aeolian dispersion can be one of the more dominant forms of contaminant transport of mining wastes in arid and semiarid climates (Sims et al.

2013). Metal-bearing dusts can be inhaled or ingested by local populations leading to chronic exposure to toxic metals, and these problems have to be addressed, together with the issue of the bioaccessibility of toxic metals, which influences their impact on health depending on the local geochemical context. To tackle the health risk, we need to go beyond the understanding of the process of contamination or exposure, and evaluate the vulnerability and capacity of societies to cope with this risk. Knowledge of the specificities of the Mediterranean mining environments is needed to design appropriate remediation actions to minimize risk to human health and to the environment.

Distribution of mining contaminations throughout the Mediterranean basin

The location and metals produced for the main European mining sites and their geological context can be found in the Metallogenic Map of Europe and Neighbouring Countries (1997). The metallic mines have been largely exploited during the nineteenth–twentieth centuries and have generated large amounts of wastes. Most of them are abandoned now. It is noticeable that mining sites are mainly located on the western borders of the Mediterranean Sea. Historically, Spain has had extensive mining activity and particularly in the eastern Pyrenees and the Beatic Cordillera on the Mediterranean border. In south of France, metal mining activities have been developed mainly in the Cevennes, the eastern Pyrenees, and the Montagne Noire regions where the last mines closed in 2004. In Italy, the main production of Pb and Zn was in Sardinia. In these three countries, deposits are found both in the Paleozoic metamorphic basement and in its Mesozoic sedimentary cover. Greece has substantial mineral resources, and large quantities of precious and base metal sulfide ore deposits are widespread along the South Aegean active volcanic arc and in Attic-Cycladic ore belt, where the famous Lavrion mine produced silver in ancient times and was one of the main industrial centers in Greece in the nineteenth century. Although Turkey has a wide variety of minerals, its resources have only been partially exploited, although exploration and mining of deposits of metals and raw materials dates back to ancient times, especially in Anatolia. Along the southern margin of the Mediterranean Sea, only Morocco, Algeria, and Tunisia have had significant deposits of Pb, Zn, Sb, Co, Fe, Mn, and Cu with most of the sites being abandoned after independence. Some mining operations are still underway in Algeria and Morocco. In these regions, metal deposits are mainly encased within carbonated layers of Mesozoic and Tertiary sediments.

Characteristics of the mining wastes

One of the main sources of contaminants is mine tailings left on site by the mine operators. Among the different types of mining wastes, those derived, after crushing to particle sizes lower than 1 mm, from the ore concentration process, are voluminous and widely distributed over mining sites. They are also most likely to be affected by weathering and erosion due to their fine granulometry and weak cohesion. These residues were usually pumped to areas near the mill site and dumped as large piles of several hundred thousand tons which were generally left without any protection against weathering and erosion. The recovery of metal particles during the concentration process was never completely efficient, and the residues often contain up to one or several percent of the metal mined, in addition to varying concentrations of associated elements among which are currently present toxic elements such as Cd and As.

Although the majority of mining sites contain only a few of these waste dumps, several mining districts are known for the accumulation of tens of millions of tons of wastes. For instance, mine wastes in the southwest of Sardinia mining district have been estimated at about 45 million m³ (Cidu et al. 2009). The “Lavadero Roberto” refining center, in Cartagena (SE Spain), used to be the biggest refining facility in Europe, has dumped more than 57 millions of tons of waste into the Mediterranean Sea from 1957 to 1990, completely filling the Portman bay which is considered like the bay the most contaminated in the entire Mediterranean (Martinez-Frias 1997; Martos-Miralles et al. 2001). In Europe, since the implementation at the national levels of the European Directive on the management of waste from extractive industries (Directive 2006/21/CE), the member states have had to carry out an inventory of the mining waste sites which might potentially cause threat to environment or population health. In addition, the ProMine Anthropogenic Concentration database is presently the updated tool for Europe (Cassard et al. 2015; <http://ptrarc.gtk.fi/Promine/default.html>). In Southern countries, such inventories have not yet been performed, but complementary information can be found from the national mining offices (ONHYM for Morocco, ORGM for Algeria, or ONMT for Tunisia).

Geological context and mineralogical evolution of mining wastes

Mined metallic ore is generally composed of sulfide minerals formed in anoxic conditions at depth. In the mining wastes exposed to oxidizing conditions, sulfide minerals are not stable and the redistribution of potentially toxic elements among secondary mineral phases during aging of

the tailings varies mainly according to the local geochemical context controlled by parent rocks. Metal-bearing sulfates are common in acidic geochemical contexts, whereas metal-bearing hydroxide, oxyhydroxide, hydroxysulfate, or carbonate phases are mainly found in neutral to basic conditions (Kimball et al. 1994). In addition, metals and metalloids may also be adsorbed onto the surfaces of these newly formed phases, thereby limiting their transfer to water (Lottermoser 2010). Such secondary phases have been described at many mining sites from the Mediterranean border regions, where large extents of carbonate bedrocks are common (Cidu et al. 2009; Garcia-Lorenzo et al. 2012), especially in Northern Maghreb, where they play an important role in metal stability. In this geochemical context, metals are mainly mobilized in particulate form (Ghorbel et al. 2010; Lavazzo et al. 2012; Boussen et al. 2013; Souissi et al. 2014).

Mechanisms of contamination transfer

Transfer of contaminants by water

Topography, texture of the soil and of the mine waste, vegetation, climate conditions, and site management are the most important factors that influence the dispersion of metals and metalloids in the particulate phase into the different compartments of ecosystems (García-Rizo et al. 1999). The torrential rainfall and the scarce vegetation, that is characteristic of these Mediterranean areas, amplify the erosion processes. Metallic contaminants are dispersed both downstream and downslope from the mining site mainly due to surface runoff, as shown by Cidu et al. (2009) who conducted a hydrogeochemical survey in two mining districts in Sardinia (Italy). Metals are usually mobilized as suspended particulate matter during flash flood events. When the kinetic energy of the system lessens, particle sedimentation occurs. Such events result in the contamination of both the bottom sediments of streams and rivers and of flooded soils (Resongles et al. 2014). The transport of particulate matter to the sea by streams and rivers has also been documented in Spain (Navarro et al. 2008). In addition, events such as the collapse of storage dams containing high heavy metals wastes into the Guadamar River (Spain) are rare, but when they happen, they are extremely polluting: The last flood deposited a 3- to 30-cm-thick layer of mining wastes over an area 40 km long and 0.4 km wide (Querol et al. 2000).

Metals and metalloids are also mobilized in the dissolved phase in watersheds of mining-related sites. High As concentrations have been evidenced in alkaline conditions at several mining sites in the Mediterranean area including in pit lakes in Zeïda, Morocco (El Hachimi et al.

2007; Benyassine et al. 2013); in the Amous River at Carnoulès, France (Casiot et al. 2009; Héry et al. 2014); and in the Baccu Locci stream catchment in Sardinia (Frau and Ardaù 2003). The enrichment is related to the anionic character of this element, which, at alkaline pH, is less efficiently sorbed than metallic cations on negatively charged iron oxyhydroxides. Also, the transfer of dissolved metals from mining sites toward the water compartment is greatly enhanced by AMD. The generation of AMD results from the oxidation of sulfides in mine waste piles and produces acid leachates containing extremely high concentrations of iron and sulfate, together with toxic metals and metalloids. In the Mediterranean area, this process is limited to a certain extent by the predominance of carbonate rocks that buffer the pH (Metallogenic Map of Europe and Neighbouring Countries 1997).

Nevertheless, there are a number of mining sites in Mediterranean countries where acid mine drainage (sometimes ephemeral after rainy events) has been evidenced like Carnoulès in France (Egal et al. 2010), Kettara in Morocco (Hakkou et al. 2008), Kirki in Greece (Papasioyi et al. 2014), Alaşehir in Turkey (Gemici 2008), Lefka-Xeros in Cyprus (Gökçekus et al. 2003), Sidi-Kamber in Algeria (Boukhalfa and Chaguer 2012), mines in the northern Apennines in Italy (Frau and Ardaù 2003), and many mines in the Iberian pyrite belt in Spain (Alcolea et al. 2012). At the Spanish sites, AMD is responsible for the permanent acidity of the Rivers Odiel and Tinto along the 60 km of their courses and for the transport of enormous quantities of dissolved metals to the estuary (Grande et al. 2014), increasing the flow of metals to the Mediterranean Sea (Elbaz-Poulichet et al. 2001).

The weathering of sulfide waste piles and the generation of AMD under the Mediterranean climate have received little attention to date. A different weathering profile has been reported in mine tailings during low water through fluxes and episodic wet–dry cycles (Hayes et al. 2014) from that under humid climates; this weathering profile is characterized by accumulation of secondary iron sulfate minerals at shallow depth in the tailing piles, whereas under humid conditions, they would have been soluble and leached with AMD (Dold and Fontboté 2001; Navarro et al. 2004); this layer of gossan material may be subject to both wind dispersion and water erosion (Hayes et al. 2014).

While sulfide mineral oxidation may be abiotic, in the presence of microorganisms involved in iron and sulfur oxidation, the reaction rate is many orders of magnitude higher (Baker and Banfield 2003; Vera et al. 2013; Dold 2014). Known iron-oxidizing species involved in the production of AMD including *Acidithiobacillus ferrooxidans* or *Leptospirillum ferrooxidans* are widely distributed throughout AMD systems (Baker and Banfield 2003; Schippers et al. 2010) and are also present in the

Mediterranean region at the Carnoulès mine in France (Bruneel et al. 2006, 2011), in the Rio Tinto river in Spain (España et al. 2007; Sánchez-Andrea et al. 2012), or in similar arid or semiarid environments like Chile (Diaby et al. 2007). However, it is not known whether the Mediterranean climate influences the rate of AMD generation and the microbial populations involved in this process. The mine water chemistry of AMD varies considerably across the world, explaining the presence of different types of microorganisms (Johnson and Hallberg 2003; Hallberg 2010). Climatic factors including temperature (Volant et al. 2014), rainfall (Edwards et al. 1999), or season (Streten-Joyce et al. 2013) have been shown to influence the structure and dynamics of microbial communities in AMD. In addition, pH is highlighted by many studies as an important factor (Kuang et al. 2012; Chen et al. 2013).

The impact of AMD on water quality in Mediterranean mining areas is highly dependent on the presence of carbonates, whose neutralization capacity counteracts the acidity produced by pyrite oxidation. Natural attenuation processes involving biotic and abiotic iron oxidation, precipitation of iron, aluminum and manganese oxyhydroxides, and sorption and co-precipitation of metals and metalloids onto newly precipitated phases (Adra et al. 2013; Maillot et al. 2013) also help to limit the dissemination of AMD-derived metals and metalloids. Microorganisms play a key role in these attenuation processes as they are involved in the biogeochemical mechanisms that control metal and metalloid speciation and behavior. At acid pH, Fe-oxidizing microorganisms, commonly found in AMD, increase the rate of Fe oxidation by several orders of magnitude, enabling the precipitation of Fe (Rowe and Johnson 2008). As-oxidizing bacteria such as *Thiomonas* have also been found to increase the efficiency of As attenuation in AMD (Bruneel et al. 2003). In contrast, some microorganisms, such as Fe- or As-reducing bacteria, have been shown to accelerate the reductive dissolution of ferric iron-containing minerals, triggering remobilization from mine contaminated riverbed sediments to the aqueous phase (Hallberg 2010; Héry et al. 2014). A better understanding of the specificity of natural AMD attenuation processes in Mediterranean mining areas, together with identification of the structure and function of microbial community involved, is of great importance to mitigate the impact of such pollution.

One major specificity of the Mediterranean climate that influences the dispersal of AMD-derived elements in the water compartment is the extended periods of drought that lead to the formation of soluble acid efflorescent salts and mine waters concentrated by evaporation in piles of mine wastes and AMD channels. These salts are rapidly dissolved, and concentrated mine waters are flushed during

the first major runoff after the dry season, leading to the discharge of acidic metal-rich fluids into surface waters, and subsequently to considerable increases in the metal concentrations. This process, known as the “first flush,” was reported by Canovas et al. (2010) in the Rio Tinto in Spain. Major seasonal variations in metal concentrations have been recorded in Mediterranean rivers downstream from AMD inputs, linked with the alternation of extended periods of drought followed by flash flood events (Casiot et al. 2009; Nieto et al. 2013).

Transfer of contaminants by wind

Wind transfer of contamination is specific to the semiarid conditions of the Mediterranean climate, and few studies have focused on this transfer mechanism, either on quantifying, or the specialization of metal-bearing particles dispersed by the wind. A few studies have addressed dust emission from active mining sites and quarries linked to crushing, grinding, or transport (Kakosimos et al. 2011). Atmospheric heavy metal deposition plumes adjacent to smelters have also been documented (Sanchez de la Campa et al. 2007). The results are used to optimize processing of the material to reduce the negative impact on surrounding areas. But in the case of abandoned mining sites, contamination dispersion by wind has only been the subject of the description of the impact of the contamination on surrounding soils (Boussen et al. 2013). Only some recent studies have focused on the characterization of air quality around ancient mining sites. At the former mining site of Lavrion (Greece), Protonotarios et al. (2002) showed that the severe soil contamination that resulted from 3000 years of mining and metallurgical activities is the source of Fe, Pb, Zn, Mn, and Cu in PM₁₀ (particulate matter with diameter of 10 micrometers or less) which concentration in air increases particularly during summer. But studies on dust emission and transfer from abandoned mining wastes are missing except for recent monitoring study of suspending particulate matter that showed that the number of exceedances of the PM₁₀ short-time limit value recorded from 2011 to 2013 reveals a critical situation for the area of Portoscuso in Sardinia (Cigagna et al. 2014). In Spain, Moreno et al. (2007) and, in Tunisia, Ghorbel et al. (2014) monitored dust emission and the transfer of suspended particulate matter from abandoned mining wastes. Both studies provided evidence that particulate matters suspended by the wind from the tailing materials are enriched in metals and metalloids of the inhalable size fraction (PM₁₀), with regulatory limits being exceeded in the villages located close to former mining sites. Besides, a survey of atmospheric heavy metal deposition in the South Marmara region (Turkey) using concentrations of metallic elements in mosses as an indication of the level of air

pollution in the region produced maps and detailed information on contamination caused by wind dispersion of metals (Coskun et al. 2011). In the Rio Tinto district (Spain), the resuspended mine waste dust contributed notably (32 %) to the total concentration of toxic trace metals into the atmosphere with the consequent impact on public health (Sanchez de la Campa et al. 2011; Castillo et al. 2013).

Finally, using a modeling approach to predict the concentrations of airborne metals and to produce spatial representations of the dispersion of contamination, Ghorbel et al. (2014) have addressed the emission of fugitive dust from the surface of mine waste dumps from the ancient mining site of Jebel Ressay in northern Tunisia. They spatialized the area in which Pb and Cd concentrations exceeded WHO (2005) guidelines during the summer season using local wind speeds and directions and found that PM₁₀ Pb and Cd concentrations in air were above guidelines for distances of up to 1200 m from the mining waste dump in the direction of the highest speed wind. This modeling approach, which has not yet been developed elsewhere in Mediterranean region and nor in other arid region, could be a useful tool for exposure to metallic contamination assessment studies.

Soil–plant transfer of contaminants in agricultural soils

High concentrations of metals can be found around abandoned and active mines, into nearby soils, food crops, and stream sediments (Lee et al. 2001; Martinez-Sanchez et al. 2012). The contamination of soils due to the presence of toxic metals may result in negative consequence, such as damage of ecosystems and agricultural productivity, and contamination of water resources (Lee et al. 2001; Wong et al. 2002; Galan et al. 2003). Exposure to these metals, through the ingestion of vegetables grown on contaminated soils, can induce human health problems.

In mining environment, there are few studies on the accumulation of metals in plants in agricultural areas, especially in Mediterranean regions; the majority of studies were carried out to find plants that could clean polluted environments (phytoremediation) (Galan et al. 2003; Monterroso et al. 2014). Usually, these sites showed unfavorable conditions for plant growth (low nutrient availability, low cation exchange capacity, limited organic matter content, and high metal concentrations) (Monterroso et al. 2014). A few references are available in the literature concerning tree species (citrus, olive trees, almond trees, date palms, quince, grape, etc.), vegetable, cereals, or plants specific to this zone (prickly pear, etc.) (Pinochet et al. 1999; Romero et al. 2012; Béjaoui et al. 2014).

The uptake of metals by plants generally depends on both the species of plant and the availability of the metal in the soil (Kabata-Pendias 2011). Metal absorption by plants occurs mainly through the roots but can also occur through leaf stomata after atmospheric deposition (Kabata-Pendias 2011). The availability of metal also depends on the total concentration of the metal in the soil, its speciation, as well as the physical–chemical conditions of the soil (mainly soil pH). In acidic soils, the metal availability is higher than in alkaline soils (Kabata-Pendias 2011). Acidic soils are most commonly found in areas where soils were formed from siliceous parental materials, in forest zones and in mining areas containing pyrite like in North Mediterranean countries (Spain, Portugal). Alkaline soils (pH above to 7.5) are found where soils were formed from carbonate-rich parental materials (Algeria, Morocco, Tunisia, and Spain).

In South Mediterranean region, a recent study was conducted in the vicinity of mining wastes from the former Jebel Ressas lead mine (Tunisia) to determine the contamination of different crops (Béjaoui et al. 2014). These agricultural soils are alkaline with Cd concentrations ranging from 0.2 to 230 mg kg⁻¹. Despite high Cd concentration in soil, very few olives had values that exceeded the European Commission standards (Commission Regulation EC 2006). In opposite, this study also showed that prickly pears, dates, grapefruits, and oranges accumulated Cd to concentrations exceeding the European Commission standards. In a similar context, Boussen et al. (2013) showed that in agricultural calcareous soils around the Pb Jalta mine (North Tunisia), in weakly contaminated soils (Cd: 1.2 mg kg⁻¹; Pb: 656 mg kg⁻¹), wheat grains showed low concentrations of Cd (0.06 mg kg⁻¹) and Pb (0.1 mg kg⁻¹), whereas in more contaminated soils (Cd: 42 mg kg⁻¹; Pb: 11,000 mg kg⁻¹) located closer to the source of pollution, wheat grains accumulated higher quantities of metals (Cd: 0.3 mg kg⁻¹; Pb: 1.3 mg kg⁻¹) that exceeded European standards (Commission Regulation EC 2006). Another study, in alkaline agricultural soils near the mining activity in La Union (Murcia, Spain), showed that Pb concentrations in Swiss chard (*Beta vulgaris*) are above the European standards (Clemente et al. 2007). These agricultural soils are mostly carbonated, with alkaline soil pH and low metal solubility (Lavazzo et al. 2012; Boussen et al. 2013), suggesting low translocation of metal to plants. Nevertheless, as plant analyses revealed accumulation of these contaminants in the edible parts, the metal uptake could result from local acidification and/or acidification of the rhizosphere by plant roots (Souissi et al. 2014).

A study realized by Candeias et al. (2013) in acidic agricultural soil around the Panasqueira mine (Portugal) showed that the As contents in the rhizosphere soils exceeded 20 times the reference value for agricultural soils

(11 mg kg⁻¹) according to the Ontario guidelines (Ministry of the Environment 2011). Vegetables grown in the nearby sites were also contaminated. Some edible plants frequently used in the region could be enriched in As, Cd, and Pb and were above the maximum permitted level for vegetables proposed by FAO. Potatoes tended to have a preferential accumulation in the leaves and roots, while in cabbages most elements had a preferential accumulation in the roots. These vegetable may represent a serious hazard if consumed (Candeias et al. 2013). However, a study realized with fruit tree (citrus) in acidic soils affected by metal sulfide exploitation in Rio Tinto mining district (Spain) showed that despite the high availability of the metals, their concentrations in citrus leaves were low (Romero et al. 2012). Calculation of the transfer factors showed the following absorption sequence: Zn > Ni > Cu > Pb > As, and no hazard was predicted even for soils with high metal contents. The major risk for agricultural use of soils appeared to be in private orchards, where vegetables could absorb bioavailable elements (Romero et al. 2012). Pinochet et al. (1999) also showed that the fruits (grape, quince) accumulated selenium and copper in concentrations lower than two fodders (alfalfa and grass) in agricultural soils located in the Valparaiso mining complexes (Chili). Thus, these studies indicate that the accumulation of metals in plants is a function of the total metal concentration in soil, soil pH, but also plant species (Romero et al. 2012). Additional studies are needed on the metal accumulations depending on the distance from the pollution source but also to identify the least accumulative agricultural plants in order to avoid any contamination of the food chain.

Exposure to metal contamination

Oxidative stress in plants in response to metal toxicity

Biochemical and physiological processes in plants are known to be affected by exposure to environmental pollutants including metals. Among the many possible physiological alterations, plant metal exposure triggers in particular oxidative stress leading to the oxidation of proteins and membrane lipids (Schützendübel and Polle 2002). Some metals are known to be redox active elements and are involved in the accumulation of oxygen free radicals through Fenton reactions leading to cell membrane alteration by peroxidative degradation of polyunsaturated fatty acids (Schützendübel and Polle 2002). Reactive oxygen species (ROS) are produced continuously under normal aerobic metabolism, and plant cells possess a well-equipped anti-oxidative defense system to maintain redox homeostasis (Foyer and Noctor 2005). Glutathione (GSH),

which has been shown to have a high affinity for metals, is considered to be the main intracellular defense against ROS in plants (Noctor et al. 2012). In response to metals, plants synthesize phytochelatins from GSH sulfur-rich peptides, and phytochelatins are known to be involved in intracellular metal binding (Cobbett and Goldsbrough 2002; Carrasco-Gil et al. 2011). However, plants challenged by harmful environmental conditions lose their ability to effectively scavenge ROS, leading to an oxidative burst. Indeed, exposure to metals leads to notable alterations in the activities of the antioxidant enzymes and also in the cellular pools of GSH and ascorbate (Schützendübel and Polle 2002). Recently, loss of cellular redox homeostasis has been demonstrated in alfalfa seedlings treated with high doses of Cd and Hg (even when the treatments were very short term) preceding cell death (Ortega-Villasante et al. 2007). Finally, the responses of plant vegetative structures to environmental pollutants have been examined at a variety of scales, from molecular to population or community rank (Calzoni et al. 2007). In particular, plants exposed to Pb suffer the disruption of several metabolic processes which leads to the decrease in biomass production, induction of leaf chlorosis, and depletion of photosynthesis rate (Gupta et al. 2013). Moreover, Cd can also alter the structure of the chloroplast, affecting photosynthesis processes and reducing stomatal conductance (Souza et al. 2011). However, even if a given level of pollution may not be high enough to elicit a response from the vegetative structures, it may seriously affect the overall reproductive potential of plants (Bergweiler and Manning 1999; Hattab et al. 2010).

Exposure of human populations to toxic metals

The impact of mining pollution on human health is well established in occupational medicine, and several diseases related to exposure to mineral particles are classified as resulting from occupational activity. Many elements present in polymetallic ores, including As, Cd, Hg, and Pb, are toxic for humans. Coal worker's pneumoconiosis and silicosis are most widespread in the Mediterranean area (Laraqui et al. 1999), but singular disease are also encountered in specific mines, including a Parkinson-like disease in manganese mines (Rodier 1955) or respiratory tract cancer in phosphate mines (Checkoway et al. 1996). As described in different mining contexts, workers exposed to metallic elements (U, Ni, Cr, Cd) or metalloid (As) are at risk of lung cancer (Hornung and Meinhardt 1987; Stayner et al. 1992; Gibb et al. 2000). In addition to well-established metallic toxicity, it has been demonstrated that inhaled crystalline silica is per se classified by IARC (International Agency for Research on Cancer) as a human carcinogen (Steenland et al. 2001). For workers, the disease

burden related to these activities is partially compensated by special care offered by the industry or by the state and by financial compensation.

In contrast with the abundant literature available for occupational medicine, in the mining context, there are few studies that evaluate environmental exposure of the surrounding population to metallic elements, especially for the most vulnerable groups such as pregnant women and children. Deleterious impacts on child neurodevelopment related to exposure to Pb and Hg have been documented in many different contexts (Jarup 2003). Arsenic induces many different cancers and may also jeopardize child development (Tchounwou et al. 2003). Cadmium exposure causes nephropathy and also disorders of bone mineral metabolism (Buchet et al. 1990). Although considered as a dietary mineral, Mn has been linked with deleterious effects on child mental performance (Bouchard et al. 2011). Because of the variety of potential toxic effects, the study of the impact on health of polymetallic exposure remains a challenge in clinical epidemiology.

Several approaches, ranging from indirect assessment to clinical evaluation, are currently used to evaluate the risk. Assessment of the risk to human health is based on knowledge of the human metabolism and environmental conditions. When the concentration of a metal in air, soil, food, water, and toxic are known, it is possible to evaluate daily intake and then compare it with known thresholds (WHO 2005, 2011). In the literature, health hazards have mainly been calculated from the doses of metal consumed via contaminated food crops, drinking water, or soil (in children, Pb poisoning is established by their hand-to-mouth and pica behaviors) (Carrizales et al. 2006; Malcoe et al. 2002). Knowledge of air quality and air pollution is a fundamental requirement to prevent risks to human health (Zou et al. 2009). Under Mediterranean climates, dusts are emitted from mining areas, and dust inhalation and ingestion are the two main pathways of exposure for local populations, leading to high intakes of toxic metals (Ghorbel et al. 2010, 2014; Argyraki 2014). Different approaches have been developed, and many metal dose-response models are available to estimate the risk of the populations concerned, including the IEUBK model (integrated exposure uptake biokinetic) which was developed by the US Environmental Protection Agency (Hogan et al. 1998). This model predicts the risk of elevated blood Pb levels in children exposed to environmental Pb from many sources. Recently, the model was used in a risk assessment study that highlighted the importance of garden soil and house dust in a village in a mining area in Northern Greece (Argyraki 2014). Other models, such as CalTOX or NORMTOX, can be adapted to a wide range of situations to evaluate exposure to many different contaminants

through multiple environmental pathways and taking into account the local geographical characteristics (Bonnard and McKone 2009; Ragas et al. 2009). In Southern countries, these models still need to be adapted to local conditions (particularly dust ingestion rates in Mediterranean conditions) to obtain accurate and reliable predictions. In mining context, the bioaccessibility of metals is a key to understanding human exposure. The chemical structure of the contaminants and associated mineral phases affect their solubility in physiologic fluids and may strongly influence the absorption capacity of children as well as adults. The Bioaccessibility Research Group of Europe (BARGE) proposed a standardized method to evaluate the metal bioaccessibility in soils contaminated by mining activities (Denys et al. 2012). In addition, a geochemical modeling approach can be used in order to understand the parameters controlling the metal bioaccessibility as described by Ghorbel et al. (2010) who have shown that, in a carbonated geological context, common in the Mediterranean regions, the solubility of metal toxic elements, such as Pb and Cd, may be controlled by precipitation of secondary carbonate minerals in digestive fluids, acting as natural protection.

In addition to such indirect approaches, surveys based on a representative sample of the population of interest were also conducted (e.g., Lewin et al. 1999). This study followed the classical epidemiology steps with calculation of the size of the required sample, random sampling, obtaining the informed consent of the interviewees, obtaining the approval of the ethical committee, etc. Such study explored risk factors associated with Pb exposure and with the spatial diffusion of the contamination. Reference biomarkers are concentrations of metals in the blood or urine (Angerer et al. 2007). In some cases, alternative biomarkers were used such as metal concentrations in the hair or nails, which provide information on chronic exposure (e.g., Barbieri et al. 2014). The classical bias of epidemiological studies has to be taken into account, especially selection and information bias that could lead to a non-representative population sample or a miss evaluation of exposure determinants or risk factors. Finally, in the case of well-organized health systems, population screening can be proposed to the people (Moodie and Evans 2011). Often voluntary and free of charge for the participants, screening aims to be exhaustive in order to identify everyone faced with the risk of exposure (American Academy of Pediatrics Committee on Environmental 2005; Dor and Denys 2011). Depending on who participates, this type of design may provide information on risk factors and on the spatial distribution of the risk, but the main aim is to identify people who are overexposed. In this case, the biomarker must have an individual well-established diagnostic value.

Regulating mining contamination: the gap between Northern and Southern Mediterranean regions

Sustainable management of polluted territories and prevention of the related health risks is a challenge for public authorities around the world (Torny 2013). In the Mediterranean regions, the main concern is exposure, sometimes on very long-term, of the populations to the waste left over from past mining activities. Former industrial sites are frequently used for residential purposes, even when no rehabilitation was undertaken or rehabilitation was insufficient, as evidenced in France (Report of the Court of Auditors 2003) but also in Tunisia (Becerra et al. 2015) and in Morocco (El Hachimi et al. 2007). Beyond the environmental impacts and related health risks, one of the challenges involved in controlling chronic contamination is the degradation of water resources for populations living in a semiarid environment and threatened by severe water shortages in the coming decades, especially in North Africa.

One of the main differences between Northern and Southern Mediterranean countries is the identification and the definition of mining waste as a public concern. First, the problem cannot be managed by the qualified public institutions if not identified and defined. Moreover, the absence of political and social identification of the environmental and sanitary-related risks is a worsening factor of social vulnerability: How can people protect themselves from a risk that has not been identified as such? As a consequence, the vulnerability to the mining contaminations is unequally distributed between Northern and Southern countries, whereas the situations in each area are more homogeneous. In Northern Mediterranean countries, the legislation is older, more developed and more operational than in Southern countries (Table 1, supplementary material). In Southern Mediterranean countries, the national qualification of mining impacts and risks (on health and environment) may not yet have been identified as a social and a public concern, as neither the mining waste nor the environmental and sanitary-related risks have specifically dedicated legislation. Mining wastes have constituted part of the environment of populations who have been exposed for several decades and are associated with discomfort rather than with health risks. For example, in Jebel Ressas (Tunisia), the inhabitants live “with” the mining wastes. As the spoil heaps of mining wastes are so familiar, they do not arouse the suspicion of the residents about their possible impacts on their own health and on the environment (Becerra et al. 2015). The contamination caused by mining wastes has not been identified or defined as a subject of collective action at the local level or as a

public issue at the national scale. In Morocco, although recent attempts to legislate aimed to prevent the risks and impacts of the mining industry, no legislation obliges the owners to rehabilitate the mining sites after mine closure. Moreover, the current legislation is not retroactive and thus conceals part of the problem of mining activity, in particular the contamination of “orphan sites,”¹ but also the socioeconomic consequences of the closing of the mine. Many abandoned mining sites were not restored and became “distressed spaces” both environmentally and socioeconomically speaking (Babi 2011).

In Northern Mediterranean countries, the risks connected with mining wastes are the subject of national and European legislations (Table 1, supplementary material) even if, in practice, the economic issues linked with mining continue to weigh heavily in the political decisions at national level. Today, the restoration and the reconversion of the mining sites are tending to be defined before industrial activities begin, in order to limit the environmental, social, and economic costs of the “post-mining” period. Indeed, at European scale, mining regulations are drawn up with the key objective of protecting the environment and human health “against the prejudicial effects caused by the collecting, transport, treatment, storage, and deposit of waste.” Following a number of mining accidents in Europe at the end of the 1990s, the reflection at scale of the EU on the management of mining waste, supported by the European Parliament, led to the publication in 2006 of Directive 2006/21/EC specifically dedicated to the management of mining waste. This directive requires owners to develop plans of waste management (to reduce, treat, and eliminate this waste) with the aim of preventing all possible hazards for health or for the environment. It also includes consultation of the citizens concerning the authorization of installations for managing mining waste. It promotes the dissemination of information to the public concerning both the authorization and operation of the extractive activities. The member states have some latitude in achieving the objectives defined, such that the implementation of the directive could vary considerably across the European territory. As in the case of other environmental issues, the application of national or European environmental standards sometimes encounters problems, as witnessed by the former Salsigne gold mine in south of France (Report of the Court of Auditors 2003) or the mining area of Cartagena—La Unión in Spain. These cases are particularly significant concerning the respective place of the

environmental (weak) and economic (priority) costs in the public decisions concerning mining waste.

The science has generally not much influence on the political decisions concerning the importance of the environmental quality and health-related risks. It can nevertheless bring answers at the operational level by helping in the rehabilitation of polluted soils and industrial sites (abandoned, closed, or still in service).

Phytostabilization as a tool to control metal pollution

In the context of mining, one major objective is to limit the transfer of contaminants from mining waste to the different components of the environment (water, soil, air, biota). To this end, planting a ground cover is one way to limit water and wind transfers to surface waters, groundwater, agricultural soils, or residential areas.

Plant growth strategies in the presence of high concentrations of metals

Plants able to proliferate in the presence of high levels of metals in the soil are called metallophytes and have developed two main strategies to prevent the toxic effects of metals in soils: exclusion or accumulation (Baker 1981). In exclusion, plants prevent the entry of metals into the roots and/or their translocation to shoots (Baker 1981; Krämer 2010). Several hypotheses have been proposed regarding the mechanism of metal exclusion including modifying the pH in the vicinity of the roots by root secretion of organic acids or metal-chelating ligands that bind metals and decrease their bioavailability, or by accumulating metals in root cell walls or in associated microorganisms, or the formation of redox and pH barriers at the plasma membrane (Taylor 1987). Exclusion by the shoot is a mechanism based on the uptake and accumulation of metals only in roots combined with a limitation of the metal translocation from roots to shoots to maintain a low metal concentration in shoots (Bulak et al. 2014). This mechanism has been identified in some Mediterranean species including *Silene paradoxa*, *Digitaria eriantha*, *Limonium monoptalum*, and *Cytisus striatus* (Murciego et al. 2007; Cambrollé et al. 2013; Colzi et al. 2014).

Accumulation refers to the ability of plants to accumulate metals. Plant metal accumulators and hyperaccumulators can be distinguished among plant species. Metal accumulators are plants that concentrate metal in the aboveground tissues, and their metal content is higher than the concentrations measured in the soil (Baker and Walker 1990), whereas the concentration of metals in the metabolically active parts of the plant is maintained at a

¹ In certain cases, it is impossible to identify the companies who own a mining site and who are consequently responsible for the contamination caused by a mine. In Northern Mediterranean countries, these abandoned “orphan sites” are generally taken over by the State. In Southern Mediterranean countries, they are generally ignored or forgotten.

low level. This can be achieved by the sequestration of metals into old leaves, in the leaf epidermis, epidermal secretory cells, vacuoles, and cell walls (Remy and Duque 2014). Finally, some plants are able to concentrate metals in enormous amounts, and plants with 50–100 times higher concentrations of the element compared with concentrations in the surrounding vegetation, and these are referred to as metal hyperaccumulators (Cappa and Pilon-Smits 2014).

Phytostabilization to restrict metal mobility

Due to the ability of plants to grow in metal-rich environments, many green technologies have been developed that are grouped together under the term “phytoremediation,” which refers to the process of decontaminating soil by using plants to absorb metal pollutants. This can take two major forms, phytoextraction (metals are concentrated in the aboveground parts of the plants) or phytostabilization (metal mobility is restricted). Phytoextraction is a very long-term process and cannot provide an immediate response to the emergency created to metal pollution, and phytostabilization cannot be considered as a method of decontamination because contaminants are still present in the soils in different forms. In addition, several factors, including the ability of plant roots to reach a certain depth in the soil, the degree of accumulation of the metals in the shoots, and the possibility of obtaining a high biomass in polluted soil, affect the efficiency of phytoextraction and consign this technology as an experimental approach. In contrast, phytostabilization means that metal soil contaminants are immobilized through absorption by roots, adsorption onto the root surface, and/or precipitation within the area of plant roots. Such plants are already used to limit the spread of metal contaminants via wind dispersion or water erosion, soil dispersion, and leaching. Plants that are tolerant to and excluders of certain metals play a fundamental role in phytostabilization strategies designed for metal mine tailings. Ideal plant candidates should be endemic to the area in which the abandoned mine is located. Some plants that are specific to Mediterranean regions, including *Alyssoides utriculata*, *Atriplex halimus*, *Cistus libanotis*, *Dittrichia viscosa*, *Hirschfeldia incana*, or *Pinus halepensis*, have already been reported to be suitable for the phytostabilization of mining sites in semiarid climates (Auguy et al. 2013; Párraga-Aguado et al. 2013; Roccotiello et al. 2014).

Phytostabilization with the help of microorganisms

The presence of plants in abandoned mine lands enhances the heterotrophic microbial community, which, in turn, promotes plant growth and metal stabilization. Nitrogen is

usually a limiting factor for plant growth on mine tailings and research and isolation of symbiotic bacteria that are resistant to metals have been the subject of several studies. Their tolerance and their use in symbiosis with the host plant may be useful for remediation of contaminated soils (Vidal et al. 2009; Nonnoi et al. 2012). *Mesorhizobium metallidurans* is a symbiotic strain isolated from the legume *Anthyllis vulneraria* naturally present on the old mine tailings at Saint Laurent le Minier (France). This bacterium has the ability to tolerate high levels of metallic contaminants, and it was demonstrated that 80 % of the nitrogen in the legume *A. vulneraria* was derived from the atmosphere through biological fixation when the plant grew in symbiosis with *M. metallidurans* (Mahieu et al. 2011). The mobilization of atmospheric nitrogen contributed to soil enrichment in this element and promoted the growth of other plant species such as metallicolous *Festuca arvernensis* (Frérot et al. 2006). Chaintreuil et al. (2007) studied *Bradyrhizobium* strains able to grow with 15 mM NiCl₂ and isolated from a legume, *Serianthes calycina*, growing on Ni-rich soils in New Caledonia. Resistance was controlled by efflux systems such as HME-RND (heavy metal resistance-nodulation-division). *Cupriavidus taiwanensis* strains isolated from *Mimosa pudica* growing on these soils also showed a high level of resistance, higher than that of the resistant strain used as model (*Cupriavidus metallidurans* CH34) (Klonowska et al. 2012). Inoculation of pea with metallicolous *Rhizobium* strain with a high level of tolerance to Ni and Zn or *A. vulneraria* with *Mesorhizobium metallidurans* was shown to reduce the metal concentration in plant shoots (Wani et al. 2008; Soussou et al. 2013).

Phytostabilization represents a promising alternative which is increasingly considered to replace remediation of contaminated soil through conventionally technologies involving excavation operations and disposal of polluted soil. If these methods have the advantage of being fast and efficient, they also have the disadvantage of being relatively expensive and lead to the disappearance of the soil with consequently a loss of ecosystems. The main limitation for the implementation of phytostabilization in Mediterranean countries concerns the water management. Although drought-tolerant plants must be used, initial irrigation is usually required to aid plant establishment (Williams and Currey 2002).

Conclusion

The Mediterranean basin has long been the scene of intensive mining activity. Exploration, extraction, and processing of metals have resulted in huge amounts of wastes that were most often left abandoned until today. The

massive accumulation of metallic contaminants is a serious threat to the environment and to human health. This context is of particular concern with respect to the Mediterranean climate, which greatly accelerates soil erosion and triggers the transfer of particulate metal contaminants by the wind or by water. The abundance of carbonate bedrocks in the Mediterranean basin, which are particularly widespread in the Southern regions, limits acid mine drainage. However, calcareous soils do not prevent metals being transferred to cultivated plants, thereby contaminating food crops. Dispersion of metal contaminants by the wind remains a major concern in the semiarid regions of the Mediterranean basin. This vector has a direct impact on agricultural soils and consequently on food production, on local residents, and on the environment near mining sites. The harmful impacts of different toxic metals on local populations are known, but studying the impact of poly-metallic exposure on health is still a challenge for clinical epidemiology. Many dose–response models exist to estimate the risk of metal contamination of local populations but need to be adapted to Mediterranean conditions.

To prevent health risks under semiarid conditions, site management is urgently required. In this context of vulnerability, phytostabilization is a green alternative approach to the containment and possibly the reduction of metal contaminants but only if the process is perfectly adapted to the Mediterranean context.

Finally, this review of polymetallic pollution produced by abandoned mines in Mediterranean regions enabled us to identify priority actions for future research:

- Inventory of abandoned mining sites (and also waste deposit from metallurgic industries, i.e., red mud deposit) could be a priority action in Southern Mediterranean countries.
- Recent works focused on the relationship between global climate change and the increasing release of contaminants to the aquatic environment (Nordstrom 2009) suggesting that the extreme climate conditions expected in the future should also be taken into account when designing remediation projects.
- The impact of environmental pollution on human health is usually tackled through the study of a single metal pollutant, but in almost all of the contaminated sites, the pollution is polymetallic. Experimental data suggest that the polymetallic component must be taken into account to precisely assess the possible effects of synergy or antagonism in these toxic cocktails. This fundamental feature is not taken into account in the majority of studies and should be addressed at all levels of approaches to environmental risks.
- Microbial communities are key factors in regulation of acid mine drainage as they are involved both in

bioleaching and in bioremediation of mine water; a better understanding of their activities is thus needed to enable their use in mitigating the impact of pollution caused by AMD in constrained Mediterranean environments.

- A special effort should be made to identify new metal-tolerant plant species particularly adapted to the soil and climate conditions in the Mediterranean basin. The choice of endemic species that fulfill the objectives of reducing pollution and visual improvement of the post-mining landscape should be preferred in phytostabilization programs.
- The long-term fate of metal contaminants in phytostabilized waste and contaminated soils has not been thoroughly explored so far. Such data are needed to evaluate the efficacy of phytostabilization in promoting plant succession and, consequently, in permanently reducing metal toxicity.
- Particular attention needs to be paid to soil microorganisms because they play an important role in plant nutrition, in stimulating plant growth, in plant resistance to stress, in redox transformation of pollutants that influence its environmental fate and toxicity, and hence in plant fitness in constrained environments. Improvement of bioassisted phytostabilization technologies is urgently required.
- Public health awareness and public information stay fundamental issues: How to communicate on invisible risks? How to communicate sanitary risks to people who often lack means to relocate or protect themselves? What may be the real impact of public information if no public action to protect people is also implemented?

Bringing about the necessary changes in legislation and its implementation, based on pertinent scientific research, particularly in Southern Mediterranean countries, is a very important step to protect people from contamination by past or possible future mining activities. However, without a real political commitment, both legislation and science will be powerless in reducing social vulnerability to environmental contamination.

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