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Chapter 11

PHYTOSTABILIZATION OF SOILS IN MINING AREAS. CASE STUDIES FROM PORTUGAL

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ABSTRACT

Soils developed on wastes from metalliferous mines or located in the vicinity of the exploration area, under the influence of the dust deposition and/or acid mine drainage, are, in general, contaminated places that need to be subjected to recovery processes. Many of the soil remediation techniques are expensive and insufficient for the task. The selection of a particular remediation process must consider the site dimensions, mine characteristics, risks for contaminant dispersion and human health, efficiency, environmental sustainability, and also meet cost requirements.

Contaminated media (air, water and soil) can be remediated with minimal environmental disturbance by phytoremediation. This technology uses plants, has marginal costs, and is non-disruptive to the landscape and to those living near the contaminated site, contributing to landscape restoration, biodiversity improvement and/or local or national economy. Phytostabilization is a particular technology of the phytoremediation techniques. It contributes to prevent the environmental spread of the contaminants by reducing its mobility and soil erosion (water and wind), and improving soil characteristics. Phytostabilization can also decrease the migration of chemical elements into surface and groundwaters.

Metalliferous mining areas are extreme environments with low pH (soils/spoils and water), high concentrations of chemical elements (potentially pollutant), soils/spoils with low nutrition capacities where plants have growing difficulties. Jales, Penedono, Braçal, Panasqueira, Aljustrel, Neves Corvo and São Domingos are metalliferous mining sites, both in north and south of river Tejo, that were analysed in order to evaluate the elemental chemical composition of soils/spoils and plants for phytostabilization purposes.

The tolerant spontaneous and/or introduced plants, adapted to the different edaphoclimatic conditions, can be used for the Portuguese mining environmental recovery with or without cost effective amendments. Spontaneous (mainly shrubs, genera *Cistus*, *Cytisus*, *Erica*, etc.) and some introduced trees (*Eucalyptus*, *Pinus*, *Quercus*, etc.) species were identified and reveal to be well adapted to soils/spoils containing high levels of total arsenic and/or lead concentrations, associated with other chemical elements (aluminium, antimony, copper, manganese, tin, zinc, etc.). Some plants as *Eucalyptus*, *Pinus* and *Arbutus unedo* can also be used with economic profit.

INTRODUCTION

Since the beginning of the human civilization mining has taken place in a small/medium scale and, more recently, has turning into a massive and global scale as the industrial era has progressing. Inactive or abandoned mining sites are, in general, contaminated places, where tailings, waters, soils and sediments can be found, that need to be subjected to recovery processes. Tailings, containing high concentrations of hazardous geochemical trace elements coupled with physical characteristics and low organic matter and nutrients content, are extreme environments that inhibit or reduce plant development, and consequently the local biodiversity. Riverbank sediments from streams flowing in the mining areas and/or their neighbourhood, are also extreme systems, especially if influenced by acid mine drainage. These sites represent hazardous environments for humans, livestock and wildlife.

The reduction of the actual or potential environmental threat to an acceptable level is the main aim of any remediation process of contaminated systems. Techniques that promote chemical/biochemical degradation of the contaminants cannot be applied to geochemical trace elements, once these cannot be destroyed. Such goal can be achieved, for the hazardous chemical elements, either by removal or isolation or by reducing the mobility, the toxicity and reactivity of the contaminants (Wood, 2001). The majority of remediation strategies are often very expensive and insufficient for the task, depending on the contaminant, extent of contamination, and remediation strategies employed (Arthur *et al*., 2005; Saier & Trevors, 2008). Phytoremediation, that uses plants and their associated rhizospheric microorganisms, is a less expensive (on average tenfold cheaper than engineering based remediation methods), noninvasive, and more publicly acceptable technology for remediation of contaminated soils, sediments, water, and air (Arthur *et al*., 2005; Pilon-Smits, 2005; Singh *et al*., 2003). This solar-driven and aesthetically pleasing ecoremediation technology is particularly suitable for large volume sites contaminated with trace elements (Raskin *et al*., 1997; Singh *et al*., 2003). It includes a variety of techniques that takes advantage of the natural ability of plants to uptake, accumulate and/or immobilize trace elements. The terminologies, classifications and definitions of the several phytoremediation treatment strategies are not yet consensual. Among the variety of literature descriptions (Arthur *et al*., 2005; Chaney *et al*., 1997; Cunningham & Ow, 1996; Raskin *et al*., 1997; Salt *et al*., 1995, 1998; Singh *et al*., 2003; Wenzel *et al*., 1999) the processes classification used by Cunningham *et al*. (1995) and Wenzel *et al*. (1999) will be combined in this chapter. The phytoremediation thecniques can be based on soils contaminants stabilization – the containment processes – or on soils decontamination as are the removal processes. Remediation of tailings and soils from mining areas, contaminated with trace elements, can be achieved by phytoextraction (a removal process) or by phytostabilization (a containment process) (Mendez & Maier, 2008a; Wong, 2003). Phytoextraction involves the use of plants for removal or reduction of the contaminants by plant uptake and translocation to the aboveground biomass, which is then harvested for processing. Phytostabilization uses plants to convert soil trace elements into less mobile forms, but not remove these elements from the contaminated site.

PHYTOSTABILIZATION

As a result of mining activities a large amount of waste rocks and tailings are deposited at land surface becoming sources of soil and water contamination, also being, often, physically instable due to the huge dimensions of tailing piles and their deep slopes. Moreover, mine areas contain, frequently, high concentrations (1 – >25 g kg^{-1}) of several hazardous chemical elements such as antimony, arsenic, cadmium, copper, lead, mercury, tungsten and zinc (Abreu *et al.*, 2007; Abreu *et al.*, 2008; Ávila *et al.*, 2008; Carbonell Barrachina *et al.*, 2004; Conesa *et al.*, 2007; Rieuwerts *et al.*, 2008; Silva *et al.*, 2005; Tavares *et al.*, 2008) where remediation by total removal of the elements is not possible. Conventional engineering type remedial approaches have proven economically prohibitive, and sometimes ecologically unfriendly. Current engineering type remediation methods for mine tailings usually involve chemical stabilization, removing and transporting the contaminated materials to a disposal facility or isolating, *in situ*, the mine wastes, and capping them with clean fill. These technologies are very expensive and in some cases can reactivate the waste materials creating conditions for increasing acid mine generation and even improvement of erosion conditions during the reclamation works. Furthermore, after excavation both the cleaned area and the repository need reclamation, besides more land is used for the removed soil deposition. Therefore, lower cost and environmental friendly alternatives must be applied for mine areas recovery.

In situ remediation techniques using abundant, rather inexpensive natural and/or industrial, agro-forestry by-products addition, combined with plants may offer an effective alternative to conventional methods (Adriano *et al*., 2004; Macías *et al*., 2007; Pilon-Smits, 2005; Tordoff *et al.*, 2000; Wong, 2003). A vegetation cover establishment on waste materials and tailings can fulfill the goals of stabilization, contaminants containment, visual improvement, and reduction or removal of the threats for wildlife and humans. From a logistical and technical standpoint, phytostabilization provides an alternative to the engineering type remedial approaches as well as phytoextraction approaches.

Phytostabilization is a remediation technology based on the use of appropriated plant species to immobilize contaminants in soil through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants, reducing or eliminating the risk to both human health and the environment (Cunningham *et al*., 1995; Padmavathiamma & Li, 2007; Pilon-Smits & Freeman, 2006; Wenzel *et al*., 1999). The main goals of this technique are: (i) to prevent chemically based processes, as contaminants transfer (partial or total) from the polluted site to adjacent soils, and surface and groundwater by an effective vegetation land cover; (ii) to develop mechanical stabilization of the soil by the plant roots; (iii) to protect the soil surface against wind and water erosion; (iv) to reduce leachates movement into the groundwater by enhanced transpiration rates; and (v) to create a pleasant visual landscape. It is also important to have in mind that contaminants translocation within plants, from roots to shoots must be reduced to avoid further transfer into the food-chain

(Mendez & Maier, 2008a; Wenzel *et al*., 1999). This technology is based on the contaminants tolerance of the plant species used for successful revegetation of the contaminated area, and implies a careful planning which includes physical and chemical analysis of waste materials and/or soils, plant selection, pot experiments and/or field trials with or without amendments use, and bioassays.

The identification of metal and metalloid tolerant plants and the knowledge of how tailings may be amended to support plant species will lead to more cost-effective mine reclamation and restoration decisions. However, this crucial information may help to save from deficient remediation, and also to save money if inexpensive amendment materials can be found to enable vegetation of mine tailings. This is the case of many fairly abundant organic and/or inorganic industrial refuses, agro-forestry and agro-alimentary by-products, especially if they are available from nearby locations, limiting their transport cost.

Amendments

Depending on the ore types, hosted ore rock, and ore processes for metal extraction, mine tailings can be composed of silty or sandy size particles as well as coarse materials as, for instance, gravel (2 – 75 mm) or even coarser in size. These characteristics, together with high hazardous chemical elements concentrations, lack of nutrients (nitrogen, phosphorous and potassium) for plant growth support, an almost total absence of organic matter and, frequently, very low pH values are, in the majority of the cases, unfavourable media for vegetation development. Nevertheless, depending on spoil materials characteristics, the addition of low cost amendments can contribute to increase organic matter content, water-holding and cation exchange capacity, pH, nutrient content as well as microbial activity and soil structure improvement. Moreover, certain amendment applications together with plant physiological processes (e.g. rhizosphere modification and/or compounds released by the roots) enhances key biogeochemical processes such as adsorption, precipitation and redox reactions that may decrease the trace elements bioavailable fraction contributing to its immobilization in the media (Adriano *et al*., 2004) and increasing weathering and pedogenic processes of the waste materials (Abreu *et al.*, 2008; Macías *et al*., 2007). The main purpose of phytostabization is not to change the trace elements total concentration but to reduce the available fraction to biota and contaminants leaching in order to lower the environmental risk (Adriano *et al*., 2004). The potential value of several amendments and their mechanisms for the immobilization of trace elements as well as case studies using different soil correctors are discussed by Adriano *et al*. (2004).

The use of mixtures of unconsolidated organic and inorganic waste materials to produce suitable amendments for degraded areas restoration, as mine tailings, is a challenge, because it combines the re-use and valuation of several wastes, originated from human activities (agriculture, industrial and municipal wastes like poultry biosolids, combustion fly ashes, sewage sludges, etc.), with the recycling of essential nutrients and stabilization of organic matter (Arbestain *et al.*, 2008a; Arbestain *et al.*, 2008b; Macías *et al*., 2007; Palumbo *et al*., 2004; Punshon *et al*., 2002). These mixtures constitute Technosols (soils whose properties and pedogenesis are dominated by their technical origin) according to the IUSS Working Group WRB (2006). The formulation of tailor-made Technosols was proposed by Macías (2004) and Macías *et al*. (2007). The correct environmental integration of these mixtures depends on the characteristics and proportions of the materials employed, that need to be well known and adequate for each purpose, as well as on the pedoclimatic conditions, types of soil/spoil to be restored (Arbestain *et al*., 2008a), and the plant species to be used (Mendez & Maier, 2008a).

The use of Technosols for sulphide mine tailings recovery has been successfully undertaken in “As Pontes Mine” and “Touro Mine” (Spain) where a good vegetation cover was accomplished together with the biological activity and biodiversity promotion. Decrease of acid water generation with the consequent improvement of the surface and underground water quality has also been observed (Macías *et al*., 2007; Monterroso *et al*., 1998).

Several environmental and social benefits are mentioned by Macías *et al*. (2007) for the use of Technosols for mine areas reclamation: reduction of the amount of wastes to be treated in specific plants and their environmental negative impact by their integration in biogeochemical cycles; reduction of energy costs for wastes management; land surface saving for wastes storing; saving on natural resources as peat and humus; saving on chemical fertilizers and a better use of nutrients contained in the used wastes; increase of biological activity and biodiversity promotion; improvement of water quality; landscape recovery by revegetation; decrease of erosion processes; economic profits from certain plant species; finally the contribution to the organic carbon stabilization and soil carbon sequestration.

The preparation of Technosols from mixtures of unconsolidated waste materials, and their behaviour and evolution, when applied in different soils/spoils and environmental conditions, must be tested to guarantee that the main soil functions (EU, 2006) are satisfied. Research in this field has been undertaken, specially to assess the contaminants bioavailability and leachability, the balance of essential nutrient elements, and the degree of stability of organic carbon forms (Arbestain *et al*., 2008a; Arbestain *et al*., 2008b; Egiarte *et al*., 2006; Yao *et al*. 2008). However, each case is a different case and the implementation of a remediation plan, by using one kind of waste or a mixture of wastes, for a specific mine area must include previous studies not only focused on the amendment or Technosol behaviour but also in the interactions between the Technosol and the tailings spoil tip. The place should be monitored for a large period of time.

Plants

Natural vegetation growth is observed in some mine sites, despite of the adverse conditions for plants establishment prevailing in those areas. These colonizing plants are completely adapted to the contaminated environments. Native and spontaneous plants in mining environments frequently show good growth rate demonstrating tolerance for toxic elements and low nutrient status, and therefore will be ideal pioneer species for natural ecological succession (Mendez *et al*., 2007; Wong, 2003). These pioneer plants have a great importance in biogeochemical cycles contributing to the soil-forming processes. Therefore, the selection of native and spontaneous plants growing in mine areas seems to be the best choice for phytostabilization purposes because, in addition, they usually show non-accumulator characteristics.

Metal-tolerant plant species have being developing great abilities to resist to the extreme conditions when compared with members of the same species from clean sites. They also can be metallophytes that have evolved on mine wastes for years (Whiting *et al*., 2004), as is the case of *Erica andevalensis* Cabezudo & Rivera an endemic species from Andévalo (Spain) whose distribution is limited to the Iberian Pyrite Belt (Abreu *et al*., 2008; Cabezudo & Rivera, 1980) or *Alyssum serpyllifolium* sbsp. *lusitanicum* Dudley & Pinto da Silva a nickel hyperaccumulator endemic to the serpentinic area from NE Portugal (Freitas *et al.*, 2004a; Lázaro *et al.*, 2006). These endemic species may become extinct as soon as their habitat changes (Aparício & Garcia-Martin, 1996; Whiting *et al*., 2004). Whiting *et al*. (2004) call attention to the need to create research priorities for identification, conservation and the understanding of ecological function of these specific plant species that have evolved to survive on metal-rich soils. The same authors sustain that such research should be strongly supported by the mine industry.

In those areas where mine soils or waste materials are naturally colonized, the plant reproduction can be improved by seed collection and sowing, as these plants correspond, frequently, to specific ecotypes well adapted to the media conditions. In the non-vegetated mine sites a search for plants growing in other sites with similar conditions, especially climatic and geochemical characteristics can be the option for a well succeed revegetation program.

The use of trees in phytostabilization of mine tailings can also be advantageous by hydraulic control due to their higher transpiration rates and deep rooting which prevents migration of leachates towards groundwater or receiving waters (Neuman & Ford, 2006; Pivetz, 2001; Schnoor, 1997). In addition, these perennial plants can have an important role in carbon sequestration and also be used for economic purposes as paper mill or for heat and energy production. However, the introduced non-native species need to be non-invasive plants to reduce any detrimental effects on the surrounding ecosystem which may affect biodiversity (Alkorta *et al*., 2004; Pilon-Smits & Freeman, 2006; Whiting *et al*., 2004). The use of genetically modified plants, a recent field of research, is nowadays also included in some programs of phytoremediaton (Pilon-Smits & Freeman, 2006). How might transgenic plants influence ecological relationships? This is a question that needs a careful research as potential risks for biodiversity conservation.

In order to establish a good ground cover or large canopy, high plant diversity, composed mainly of native species, belonging to different functional groups, with diverse root systems (from deeply to shallow rooting) performing different roles, should be the general requirements for phytostabilization. The initial vegetation cover of mine tailings by tolerant pioneer plants should serve as the basis for a successional development which leaves the site with a diverse, self-sustaining, vegetative cap that acts as a barrier for physical contact and minimizes eolian dispersion, water erosion and leaching processes (Mench, 2005; Mendez & Maier, 2008a).

The capacity for trace metals accumulation by plants can be estimated by the soil–plant transfer coefficient (TC = [total element] in shoot tissue/[total element] in mine soil or tailing), which evaluates the transference from soil to plant and represents the capacity of a species to accumulate the element. The majority of plant species have a TC < 1 for trace elements, but some few plants can be considered accumulators when TC > 1. Plants used for phytostabilization should present a soil–plant coefficient transfer – TC < 1. The ratio [total element] in shoot tissue/[total element] in root tissue should also be < 1. The hazardous chemical elements concentration in the aboveground part of the plants should not exceed the domestic animal toxicity limits to prevent exposure of foraging or wild animals (Mendez & Maier, 2008a; 2008b; Wood *et al.*, 1995).

Microorganisms

The development of soil microbiological processes, relative to bacteria and mycorrhizae in the rizosphere zone, promoting, for instance, nitrogen fixation and nutrient cycling, may contribute to achieve a low-maintenance vegetation cover. However, soil microorganisms may either increase or decrease metal/metalloid solubility (Wenzel, 2008), as they mediate the various biochemical transformations in the root zone, including redox reactions and chemical speciation (Adriano *et al.*, 2004; Wenzel, 2008). Among the soil microorganisms the mycorrhizal fungi may contribute directly to plant establishment by improving soil structure, organic matter and nutrient absorption capacity of root systems (Requena *et al.*, 2001), and modifying contaminants bioavailability in several ways, such as binding metals to fungal hyphae, thus reducing their translocation to the shoots of the host plants (Galli *et al.*, 1994; Jentschke & Goldbold, 2000; Shetty *et al.*, 1994; Tordoff *et al.*, 2000; Wenzel, 2008). However, Fomina *et al.* (2005) and Martino *et al.* (2003) demonstrate that some mycorrhizal fungi can also promote solubilization of minerals containing hazardous trace elements despite of their metal tolerance. Some bacteria can also increase the accumulation of some metals in the root and shoot plant systems by increasing the concentration of water soluble metals fraction (Rajkumar *et al.*, 2008). The plant roots protection from desiccation under severe draught stress when in symbiosis with mycorrhizas was reported by Jany *et al.* (2003). This symbiotic roots protection can be used in unfavourable media as coarse mine tailings under arid or semi arid environments. Studies concerning bacteria and mycorrhizal colonization in metal/metalloid tolerant and/or accumulator plants have been reported by several authors (Glick, 2003; Gonçalves *et al.*, 1997; 2001; Hetrick *et al.*, 1994; Portugal *et al.*, 2004; Rajkumar *et al.*, 2008; Roy *et al.*, 2007; Shetty *et al.*, 1995; Turnau *et al.*, 2007; Van Tichelen *et al.*, 2001).

Mine soils remediation can be more successful if tolerant plants are associated with efficient microorganisms that can tolerate and modify the solubility of trace elements, improve physical and chemical characteristics in the rhizospheric zone of the substratum media creating conditions to plant succession initiation.

Despite of the surveying on bacteria and mycorrhizal colonization in metal/metalloid tolerant plants further research is need on the role of both bacteria and fungi in phytoremediation processes (Jentschke & Goldbold, 2000; Nabais *et al.*, 2007; Wenzel *et al.*, 2008).

Phytostabilization practices using the adequate selection of metal/metalloid tolerant plants may benefit from soil microbial processes, but in turn may also influence the composition and function of the microbial consortia in the plant rhizosphere which may be crucial for its success (Wenzel, 2008). The identification of geoclimatic specific native plants with interesting microbial consortia, and not hazardous chemical elements accumulators in the aboveground tissues is then a challenge.

Advantages and Limitations

Phytostabilization present several advantages when compared to other classical remediation practices such as capping, excavation, or even phytoextraction. It is economically viable, less expensive once it is solar-powered, energy efficient, self-regulating, absorb carbon dioxide, and can be applied to treat sites with a polymetal contamination as mine sites usually are (Mench, 2005; Saier & Trevors, 2008). It is less disruptive to the environment, reduce the risk of contaminants spreading by avoiding excavation and transport of polluted media, and it is more aesthetics, with a high probability of public acceptance (Mench, 2005; Pilon-Smits & Freeman, 2006; Singh *et al*., 2003). Disposal of hazardous materials or biomass is not required. The microbial activity associated with plant roots as well as root exudates may contribute to immobilize chemical elements, and accelerate weathering processes aiding soil formation. Also the increase of soil organic matter due to plant establishment improves soil fertility and ecosystem restoration is enhanced by the vegetation (Macías *et al*., 2007; Mench, 2005; Mendez *et al.*, 2007). The low trace elements content in shoots, which eliminate the necessity of treatment, together with a potential high yielding biomass that can be used for different purposes (e.g. heat and energy production, paper mill production, etc.) can provide an additional source for local or national economy (Mench, 2005; Saier & Trevors, 2008).

However, some limitations can be mentioned to phytostabilization, especially in mine areas. Phytostabilization is dependent on climatic conditions, physical, chemical and mineralogical characteristics of the tailings, and permanence of amendment effectiveness that regulate plant establishment and growth (Mench, 2005; Mendez & Maier, 2008a; 2008b; Pilon-Smits & Freeman, 2006). Guidance for long-term maintenance, biomonitoring and ecological consequences of phytostabilization practices is, in general, not available (Mench, 2005). Frequently, there is a lack of information about the long-term fate of trace elements some years after a phytostabilization program implementation. However, such information is needed in order to access the efficiency of phytostabilization in reducing hazardous chemical elements leaching permanently, in improving the characteristics of tailings materials, in increasing the plant succession, and soil formation rate (Macías *et al*., 2007; Mendez & Maier, 2008a).

PORTUGUESE MINE ACTIVITY – HISTORICAL VIEW

In the territory that corresponds nowadays to the place of Portugal there is evidence that mineral exploration comes from prehistorical times. Large uncertainty exists on dating, however it is accepted that there was some mining activity in the Palaeolithic age (600 000 – 8 000 B.C.) likewise to other places of the Iberian Peninsula.

During Roman occupation (II B.C. – V A.D.), mines were extensively exploited, being copper, gold, lead, silver and tin the most important metals, as it is testified by the large amount of artefacts (lights (“lucernas”), two bronze tables from Aljustrel called Vipasca I and Vipasca II that contain roman mining legislation from Adrian times (117 – 138 A. D.)) (Domergue, 1983; Fabião, 1993), scoria, and also the presence of underground mining works (shafts and galleries some of them lined with oak, chestnut-tree or arbutus-tree wood planks) found in several mines (e.g. São Domingos, Aljustrel, Caveira, and Braçal) (Fabião, 1993; Matos & Martins, 2006; Matos *et al*., 2003). Mining activity decreased after the decay of the Roman Empire, and was substituted by a surface gathering in the Visigoth and Moors periods.

During the first centuries of the Portuguese monarchy (XII – XIV centuries) there was no specific mining legislation. The first *Law of Mines* was published in 1434 following the Roman and consuetudinary laws. As a consequence of the overseas discoveries, the mining activities, in the XVII and XVIII centuries, weakened very deeply in the inland Portuguese territory, owing to the development of mining industries in the new overseas territories (Santos & Magalhães, 1999). Gold, iron and tin were the most important exploited metals from the beginning of the Portuguese nation (year of 1143) until the middle of XXth century. For instance, in the first three decades of the XVIth century the average annual production of tin was about thirteen tons. Silver, lead, copper, antimony and mercury were more discontinuously exploited all these years long.

In the XIXth century there was an increase in the Portuguese mining exploitation. The “Commission of Mines” was created in 1850 that lasted until 1852, and was also published the general Law of Mines in December 1852. According to Leal (1875) there were registered approximately 300 mine sites, in 1867.

During the first half of the XXth century the Portuguese mining richness was concentrated on copper, iron, lead, radium, tin, tungsten and uranium. After the 1950’s the majority of the mines were closed as a result of a combination of events – ore exhaustion or the existence of low grade ores, small dimension, out of date technologies, low ore prices in the international market – and by the end of the XXth century the mining activity was reduced to the exploitation of two or three mines.

On surveying the history of the Portuguese mining exploitations there are chemical elements that deserve special mention owing to their historical and economical importance: copper, tin, tungsten, gold, radium/uranium, and antimony.

Copper

Copper has been exploited in the territory of Portugal since the beginning of the third millennium B.C., and has been exploited all along the history of Portugal mainly in the South Portuguese Zone, in the renowned Iberian Pyrite Belt (IPB), the most important massive sulphide metallogenetic province in the world, were roman remains are often found (Matos & Martins, 2006; Matos *et al*., 2003; Matos *et al*., 2008). The Iberian Pyrite Belt consists of Devonian to Carboniferous volcanic and sedimentary rocks containing locally massive polymetallic sulphide deposits forming an arched belt. This area is about 250 km long and up to 60 km wide extending from Lousal, near the Atlantic coast in Portugal to Aznalcóllar, near Sevilla in Spain (Barriga *et al*., 1997) (Fig 1.). Some of the most important deposits in the Portuguese IPB are in an abandoned state (*e.g.* São Domingos, Chança, Lousal, Caveira, Cercal, Montinho, Salgadinho), however it is possible to find deposits undergoing mining activity (*e.g.* Neves Corvo) or beginning to be exploited again (*e.g.* Aljustrel), and still not exploited deposits (*e.g.* Lagoa Salgada) (Leistel *et al*., 1998). Neves Corvo, discovered in 1977, whose exploitation began in October 1988 mainly for copper and tin, and still continuing operating in 2008, is considered one of the main European copper mine and world famous deposit (Fig. 1). The exploitation undertaken in this mine is considered a world model. It shows that it is possible to harmonize the mining activity with environment preservation values.

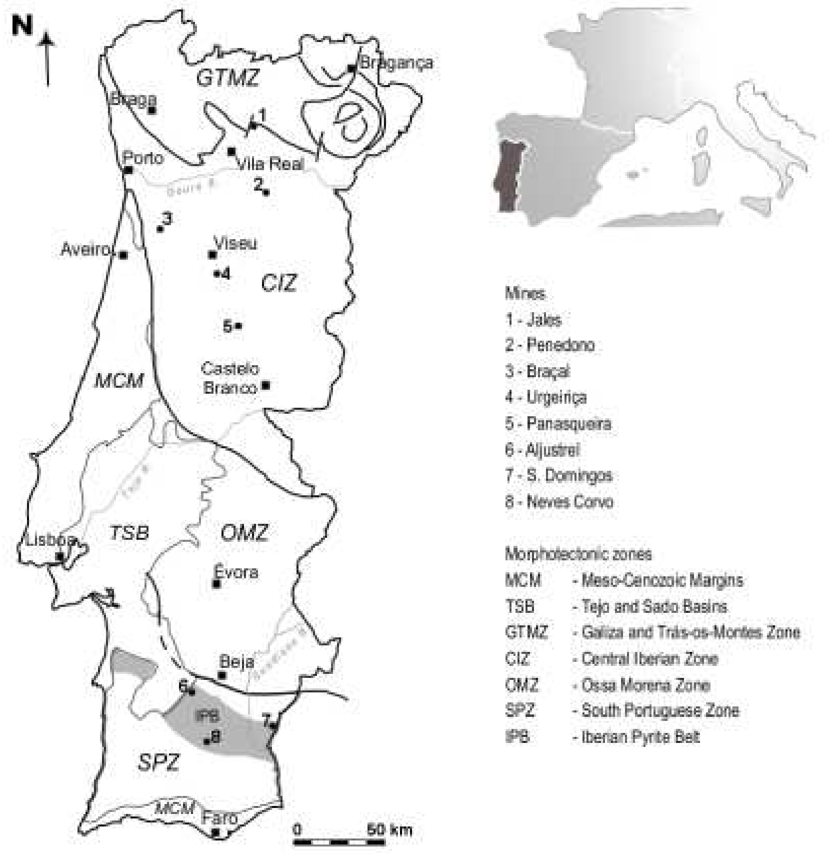

Figure 1. Map of Portugal showing the main geomorphotectonic zones and the location of some mines.

Tin and Tungsten

The Iberian Peninsula has also been an important supplier of tin for the Mediterranean and north Europe people since the Iberian early bronze age around 2 000 B.C.. The exploitation and trading, in and from the Iberian Peninsula, was done by the successive peoples that were settled nearby the ore occurrences and the peoples that domain the trade in the Mediterranean Sea and Atlantic Ocean. Tartessians were a south settled Iberian culture that traded tin (important for bronze alloy) with Phoenicians. The fall of the Tartessian culture, around 600 B.C., originate a culture shift in the south of the present territory of Portugal that went on as the domain of the Mediterranean area successively changed from Phoenicians to Carthaginian, and to Roman.

The Portuguese tin occurrences are mainly concentrated in two geologic, geotectonic and metallogenic zones: the Central Iberian and the South Portuguese Zones (Fig. 1). In the Central Iberian Zone tin is mainly associated with tungsten while in the South Portuguese Zone it is mainly associated with copper (Oliveira *et al.*, 2002). The paradigmatic mining sites for the association of tin and copper is the already referred Neves Corvo mine, and for the tin and tungsten associations can be referred the famous Panasqueira mine (Fig. 1). Records of exploitation in Panasqueira mine go up to roman times, continuing during Moors presence, and tin collection, probably, went on until the XIXth century. By the end of the XIX century this mine began to be exploited mainly for tungsten, being considered nowadays as the most famous volframite mine, and the main European tungsten producer, as a result of the quantity and quality of the ore. Besides tungsten in Panasqueira is, nowadays, also exploited tin and copper (Cavey & Gunning, 2006).

Gold

Gold started to be worked in Iberia on the same time than copper, in the earliest phase of copper age that is considered to be around 3 000 B.C.. The majority of this gold should be from alluvial sources.

The Iberian Peninsula was one important gold supplier of Rome. Mining activities had a great development during Roman times, and gold was exploited mainly in the Central Iberian Zone, Iberian Pyrite Belt, and in the alluvium materials of some rivers. Its surface and underground exploitation went on until the end of the XXth century when all the mines were abandoned.

In Adiça, some 15 km south from Lisboa, there was, still in the beginning of the XXth century, an important surface exploitation search for gold, in the ancient alluvium materials (Pliocene) of the Pre-Tejo river. Jales was an important underground Portuguese gold mine, located in the Central Iberian Zone (Fig. 1), and was one of the last gold mines to be abandoned in 1993.

Radium and Uranium

Uranium and radium mines are located in the Central Iberian Zone and their exploitation began in 1907. From 1907 to 1944 the mines were exploited for radium whose ore was treated first in France and since 1932 in Portugal, which had developed a new method that allowed the decrease of the radium price in the market. Until 1944 the uranium rich ore was discarded and was only since 1944 that the production was centred on uranium, owing to the increase of its importance and demand. The exploitation was dispersed for a large number of small mining sites, being the majority of the treatment of the ore for uranium centralized at the Urgeiriça mine (Fig. 1). The uranium exploitation in Portugal ceased around year 2000.

Antimony

Most of the antimony deposits are located nearby Porto in the Central Iberian Zone, and in the Bragança district that is mainly in the Galiza and Trás-os-Montes Zone (Fig. 1) (Neiva *et al*., 2008), but can be found in mine sites spread all over the country (Oliveira *et al*., 2002). In the Central Iberian Zone antimony is mainly associated with gold while in the Galiza and Trás-os-Montes Zone antimony is found in lead-antimony-quartz veins. Throughout the history of Portugal there are references to antimony exploitation, probably due to its association with gold and use in cosmetics. However, antimony from the Porto region mines was mostly exploited in the XIXth century, and the other mines have been exploited during the XXth century. By the end of the XIXth century there were registered 63 antimony areas from the Porto region (Neiva *et al*., 2008), but by the end of the XXth century there was no record of antimony exploitation, in spite of its presence in the ores of Neves Corvo mine (Benzaazoua *et al*., 2002) and its industrial importance.

PORTUGUESE ABANDONED MINES REMEDIATION

As a consequence of the abandon of mining activities chemical, physical and landscape impacts are observed in the mine areas. The most common visual impact arises from abandoned mining infrastructures (*e.g.* processing, cementation, and extractive metallurgy plants), huge quantities of tailings, water dams and open pits with acid water, deep coloured streams resulting from acid mining drainage, and a lack of vegetation. Tailings can be submitted to water and air erosion, which spread materials into soils and water in the vicinity of the mine area. Anomalous concentrations of hazardous chemical elements can be found in many of the waste materials, soils, stream sediments and waters.

Since 1998, the Portuguese Geological Survey (Laboratório Nacional de Energia e Geologia – LNEG, former IGM) and EDM (Empresa de Desenvolvimento Mineiro (Mining Development Company)) are surveying and characterizing the old and abandoned mines in order to access their level of environmental risk. The assessment of the environmental impact of 175 mine sites enabled to list them according to their degree of harmfulness and hazard (Oliveira *et al*., 2002). Remediation actions, mainly engineering interventions to physical stabilization of the tailings and heap dumps, are already taking place in some of the most harmful mining areas.

Remediation methodologies, other than engineering stabilization, need more detailed studies, in order to characterize and evaluate the impact of former mining on soil, water, sediments, and local vegetation (native and introduced) growing in mining areas. Some projects related with the application of phytoremediation into specific mine areas, are being undertaken (Abreu *et al*., 2007; 2008; Alvarenga *et al*., 2004; Freitas *et al*., 2004b; Mench *et al*., 2003; MINEO project (Quental *et al*., 2002); Pratas *et al*., 2005; Santos, 2007; UTPIA project (Martins *et al*., 2008). Preliminary results suggest that some plant species, especially native ones, can be used in remediation programs in contaminated areas like mining sites. However, field applications of this remediation technique in mining areas are very scarce.

PHYTOSTABILIZATION — STUDY CASES FROM PORTUGAL

Evaluation of hazardous chemical elements concentrations in soils, sediments and waste materials, and also a survey of the plant species growing in mining areas have been done in different places from Portugal. Several species can be used, with or without soil amendments, in programs of mining areas rehabilitation. These plants are well adapted to extreme environments – low soil pH, high concentration of minor and trace elements, and low nutritional soil conditions – present a good biomass production, and create a dense vegetative cap.

The mines analysed in this chapter – Jales, Penedono, Braçal, Panasqueira, Aljustrel, Neves Corvo and São Domingos – can be assembled by climatic conditions in two main territory divisions, considering the mean annual precipitation: north of the river Tejo, with annual rainfall higher than 950-1000 mm with the exception of some small areas near the border with Spain where annual rainfall lies between 500 and 800 mm; and south of river Tejo where mean annual rainfall lies between 400 to 700 mm.

North of the River Tejo Mining Sites

Jales Mine

Located in the Central Iberian Zone, at some 25 km northeast of Vila Real (Fig. 1), the Jales gold mine dates, as well as other Portuguese mines, from Roman times, and was intensively exploited from 1933 to 1993. During the XXth century, 25 Mg of gold and 100 Mg of silver were recovered. As a result of the metallurgical works a waste dump composed of 50 Gg of fine materials covered a 14.4 ha area. These materials contain high concentrations of arsenic (2960 mg kg^{-1}) and of several metals as cadmium (29 mg kg^{-1}), copper (67 mg kg^{-1}), lead (810 mg kg^{-1}), manganese (438 mg kg^{-1}) and zinc (1150 mg kg^{-1}) (Oliveira *et al.*, 1998; 2001). Water and wind erosion of these waste materials were responsible for the contaminants spread into the surface water system, sediments and soils of the mine neighbourhood. Geotechnical and hydrochemical studies showed physical instability of the tailings, and low pH and high concentrations of arsenic, cadmium, lead, manganese, selenium, zinc and sulphate in seepage water (Oliveira & Ávila, 1995; Oliveira *et al.*, 1998; 2001).

Contamination of the mine area had an impact on the health of the adjacent human population. High prevalence of eye irritation, and mucous and respiratory irritation symptoms were reported by Coelho *et al.* (2007). In the blood of the local inhabitants were also found high levels of cadmium and lead, being the cadmium blood levels correlated with the high prevalence of sensorial symptoms (asnomia) (Coelho *et al.*, 2007).

A plan for the waste dump recovery was then urgent. Under the European framework of the PHYTOREHAB project a strategy using metal tolerant plants combined with specific amendments was undertaken from 1997 till 2004. The goal was to phytostabilize the waste materials by using different spoil amendments and endemic metal tolerant plants (Mench *et al.*, 1999). These studies comprised field experiments (experimental plots) as well as lysimeters and pot experiments. The main objectives were to immobilize hazardous chemical elements and provide an effective vegetation cover of the substratum preventing migration of the contaminants to the surrounding ecosystems (Bleeker *et al.*, 1999; 2002; Mench *et al.*, 1999; 2003). In these studies were used additives that combine different potential development of chemical elements immobilization as pH increase, adsorption, complexation reactions, precipitation reactions (Adriano *et al.*, 2004) or even improvement of plant nutritional conditions. The main additives were: organic compost (C); Beringite (B), a mixture of modified alumino-silicates (pH 11) from the former coal mine of Beringen (Belgium); steel shots (S), an industrial material (pH 8.5) used for shaping metal surfaces containing mainly iron (97%) and native impurities such as manganese (Bleeker *et al.*, 1999; 2002; Mench *et al.*, 1999; 2003). Other studies, focusing microbial biomass and activity, enzyme activities, and composition of microbial community in Jales waste materials after amendment and plant growth, were also done (Renella *et al.*, 2008).

Plants that sparsely colonized the Jales mine spoils were identified and used for revegetation purposes in field and lysimeters studies. Grasses species were the main vegetation identified (*Holcus lanatus* L., *Agrostis castellana* Boiss. & Reuter. and *Agrostis delicatula* Pourex ex Lapeyr) but some specimens of *Cytisus striatus* (Hill.) Rothm were also found (Assunção *et al.*, 1999; Bleeker *et al.*, 2003).

Another pot experimental study was undertaken by Bleeker *et al.* (2003) using a mixture of Jales mine spoil with industrial sugar residue, consisting largely of precipitated calcium carbonate in different concentrations, and *Holcus lanatus* and *Phaseolus vulgaris* L. as plants. The main objective of this pot experiment was to evaluate the possible ameliorating effect of the amendment and the plant performance.

The main results obtained by the above mentioned authors concluded that the addition of organic matter in combination with Beringite and/or steel shots to Jales mine spoils resulted in a soil pH increase (depending on the amendement amount in the experiment) and a decrease of cadmium, copper and zinc mobility. However, arsenic, the main spoil contaminant, increased mobility with amendments addition (Table 1). Growth and biomass production of tolerant plants was improved as well as plant species richness and microbial activity. A decrease in arsenic aboveground biomass was also observed.

Table 1. Concentrations of arsenic and trace metals, in leachates collected in 2000 lysimeters experiments (L) with Jales spoil untreated and amended with organic compost and Beringite (CB), organic compost and steel shots (CS), organic compost, Beringuite and steel shots (CBS) (adapted from Mench *et al.*, 2003), and water-extractable arsenic and $Ca(NO_3)$-extractable metals in Jales spoil untreated and amended with different levels of Industrial Sugar Residue (ISR) (adapted from Bleeker *et al.*, 2003)

	As	Cd	Cu	Pb	Zn
	Leachates from lysimeters experiments (µg L^{-1})				
Untreated spoil (L)	36	781	3475	26	36600
CB (L)	4435	3	34	4	177
CS (L)	4255	2	27	9	55
CBS (L)	1305	1	16	2	33
	*Extractable fraction (mg kg^{-1}) DW**				
Untreated spoil	0.33	0.26	3.34	0.27	7.26
IRS 2	2.52	0.01	1.77	0.04	0.75
IRS 3.75	4.32	0.01	1.14	0.10	0.37
IRS 5.5	7.52	0.01	1.03	0.06	0.36

* DW – dry weight

Despite of those studies, a rehabilitation program took place between June 2002 and June 2003 by the Empresa de Desenvolvimento Mineiro (EDM) based on an engineering plan developed by COBA (Oliveira *et al.*, 2001; Pereira *et al.*, 2005).The principal goals to achieve with this program were the geotechnical stabilization of the tailings, and to cease wind and water erosion processes together with reduction of water, air and soil contamination. The waste materials were excavated and embanked, and then covered with a layered system consisting of (from the bottom to the top): geotextile membrane; an impermeable geomembrane (2 mm thick) of high density polystyrene covering an area of 112100 m^2 in order to isolate the waste materials and avoid contaminants spread; a bentonite layer; a 0.50 m thick sandy drain layer; geotextile membrane; a 0.80 m thick layer of inert soil (mainly weathered granite materials); and a 0.20 m thick layer of organic soil (Pereira *et al*., 2005). Drainage systems (superficial and underground) were also made. Finally, a hydrosowing of grass seeds was done. The recovered area was enclosed by a 1235 m long wire netting fence and interdicted to the public.

In October 2005, during a visit to the recovered Jales tailing it was noticed that the organic matter was strongly lost and the sparsely vegetation consists mainly of *Cytisus striatus* (Fig. 2). Several *Pinus* spp seedlings also began to grow but, as the tree root system (deep taproot that can attain more than 3 meters) development could represent a risk to the geomembrane disruption, they have been successively removed. This situation cannot be self sustainable as the surroundings of Jales tailings pile are mainly forested with pine trees.

Figure 2. Jales mine area – Engeneering recovered tailings pile with sparsely vegetation composed mainly by *Cytisus* spp

In order to evaluate the efficiency of restoration measures in Jales mine area an *in situ* bioassays with *Chironomus riparius* larvae was conducted during 2002 to 2004 by Faria *et al*. (2008) in the stream that drains the main area. A decrease in trace elements concentrations was observed from 2002 to 2004 in the water and sediments, as well as a decrease in the inhibition of larval growth. A comparison between these data and the results obtained in 1995 by Oliveira *et al*. (1998) showed also a decrease of trace elements concentrations in the water and sediments (Table 2). However, the rehabilitation program was not sufficient to eliminate the ecological impairment in the stream draining the mine area (Faria *et al*., 2008).

In conclusion, assisted phytostabilization of Jales waste materials based on suitable amendments and tolerant plant species growing in the area could be possible. However, while the treatment and amendment of the wastes reduced the mobility of several metals (cadmium, copper, lead, zinc), the arsenic mobility was higher in treated wastes than in untreated spoils.

Consequently other amendments should be tested especially focused on arsenic immobilization.

Table 2. Concentrations of arsenic and trace metals in surface water and sediments of the stream that drains the Jales mine area collected in 1995 (minimum and maximum; water sampling points n=12; sediments sampling points n=33) (adapted from Oliveira *et al*., 1998) and 2002, 2003 and 2004 (means, n=5 for the same sampling point) (adapted from Faria *et al*., 2008)

	As	Cd	Cu	Pb	Zn
Surface water (mg L^{-1})					
1995	< 0.05	0.001–0.27	–	0.01–0.06	0.01–17.3
2002	na	0.01	nd	na	1.16
2003	1.04	0.01	nd	nd	0.95
2004	0.95	0.01	nd	nd	0.60
Sediments (mg kg^{-1} DW)					
1995	502	5	22	166	191
2002	29.1	0.07	0.20	4.12	3.64
2003	17.7	0.02	0.15	2.05	1.21
2004	11.4	0.02	0.11	1.22	0.96

na = not analysed; nd = not detected; DW – dry weight

Penedono Mine

The Santo António – Penedono abandoned mine, is located in the east hill side of the "Serra da Laboreira", some 3 km northwest of Penedono village, northern central east part of Portugal, about 300 km northeast of Lisboa (Fig. 1). The mine area overlooks a valley where small villages such as Granja and Póvoa da Penela are located and whose populations live mainly from agriculture.

Mining works goes back to Roman times and there is evidence that the veins gold deposits have been mined down about 20 – 30 m. Penedono, which belongs to the Central Iberian Morphotectonic Zone, was a very important gold and arsenic mining centre in the middle fifties of the XX century. The first investigations for gold were implemented in 1930 – 1940 by excavation of old pits and shafts. The exploitation began in 1947 and ran continuously, following a hydrometallurgical process conjugated with gold cyanide extraction, until 1957 when it ceased due to the gold low price, problems with land rights and inadequate technology. Later, in the seventies, gold was extracted by copelation from the waste dump sandy materials (Matias *et al*., 2003). As much as 110 Gg of material were processed with about 331 kg of gold recovered (Saywell, 2007).

During the end of the 1990 the Rio Narcea Gold Mines company started prospecting campaigns and research work for gold (Gomes & Castelo-Branco, 2003). Since 2007 Colt Resources (COLT-C), which acquires the property from Rio Narcea Gold Mines (now part of Lundin Mining (LUN-T, LMC-N)), is drilling in the Penedono concession (Saywell, 2007). According to Saywell (2007) the results from the surface rock and underground sampling of core done by Rio Narcea showed that it was possible to obtain values ranging from 2.28 to

16.03 g of gold per Mg. Due to the gold high prices in the current market Penedono mine can be reactivated.

At Santo António the mineralization is characterized by steeply dipping quartz/sulphide gold-bearing veins. Quartz veins are settled in shear fracture zones crossing hercynian granite rocks. Besides quartz, the veins are rich in arsenopyrite, pyrite, galena, sphalerite, chalcopyrite, ferberite, and bismuthinite. Secondary minerals as covelite and scorodite were also identified (Sousa & Ramos, 1991). The veins gold grade and the content of gold are dependent upon the amount of arsenopyrite (Saywell, 2007).

Nowadays, the mining complex composed of several infrastructures as a decaying mill, two rusted ball-rod mills, a chimney, a tailing pond, and four tailing piles are abandoned and present a high level of physical degradation. Two of the four waste dumps are composed of fine siliceous sandy materials presenting stratified clay-loam material yellow-orange and blue-green in colour. These two waste dumps, are sparsely or, in some zones, more intensely colonized by vegetation. They are crossed by a large and deep gully being under strong water and wind erosion (Fig. 3). The other dumps contain various materials, including black muds, and one of them is relatively well stabilized by vegetation (Fig. 4). The abandoned waste dumps showed high total concentrations of arsenic, gold and silver and medium to high contents in copper, lead, manganese, and zinc (Table 3); bismuth is also present with concentrations ranging from 42 to 788 mg kg^{-1} (Abreu *et al.*, 2007; Matias *et al.*, 2003). Scorodite, olivenite, simplesite, gypsum, muscovite, quartz and iron oxides are some of the minerals that can be found in waste materials, some crusts developed above them or nearby the chimney and dumps (Matias *et al.*, 2003).

Figure 3. Penedono mine area — waste dumps, sparsely or, in some zones, more intensely colonized by *Cytisus* spp., *Pinus pinaster* and *Castanea sativa* trees, etc.. Bared dumps are crossed by a deep gully.

The surface waters from the surrounding area of the mine were characteristic of granite environments – acidic with low electrical conductivity and mineralization. Waters that drained the tailing piles (leachate) presented the lowest pH, high electrical conductivity, high concentrations of dissolved aluminium, arsenic, sulphate, and other trace elements, as is shown in Table 4 (Matias *et al.*, 2003; Matias *et al.*, 2006). These seepage waters, together with dust material removed by wind from the tailings, are responsible for the spread of hazardous chemical elements, particularly the arsenic, from the mine wastes, in the surrounding soils.

Table 3. Statistics of concentrations of chemical elements in tailings (DW) from Penedono mine area (adapted from Abreu *et al*., 2007; Matias *et al*., 2003)

	Ag mg kg^{-1}	Al g kg^{-1}	Au mg kg^{-1}	As g kg^{-1}	Cu mg kg^{-1}	Fe g kg^{-1}	Pb mg kg^{-1}	S g kg^{-1}	W mg kg^{-1}	Zn mg kg^{-1}
Geom. mean	7.14	22.64	2.98	26.57	188	75.02	237	3.95	165	76
Minimum	1.90	13.57	1.18	10.40	29	28.66	73	0.56	< dl	18
Maximum	37.14	34.01	10.60	53.90	734	258.4	959	25.52	258	294

< dl – lower than detection limite of the instrument; DW – dry weight

Table 4. Concentrations (mg L^{-1}) of sulphate, arsenic and trace metals, pH and electrical conductivity (EC µS/cm) in surface and seepage water from the Penedono mine area (adapted from Matias *et al*., 2003; 2006)

	pH	EC	SO_4^{2-}	Al	As	Cu	Fe	Mn	Zn
				Surface water					
Geom. mean	5.23	42	3.82	0.300	0.012	0.032	0.019	0.136	< dl*
Min.	4.42	30	0.24	0.136	0.001	0.013	0.004	0.099	< dl
Max.	6.73	67	19.95	1.060	0.078	0.079	0.057	0.188	< dl
				Seepage water					
Geom. mean	3.55	916.4	520.79	36.00	0.418	0.937	1.836	4.859	1.219
Min.	2.58	289	111.20	7.87	0.006	0.241	0.019	0.469	0.093
Max.	4.24	4300	2644	130	122	2.900	690	19.600	5.100

* < dl – lower than detection limite of the instrument

However, the contamination seems to be limited to a relative restricted area. In fact, though the surface and seepage waters drain to the Granja stream there is no negative influence in the stream water, which presented pH between 5.95 and 6.33, and low values for the electrical conductivity and sulphate concentration. Also arsenic and hazardous chemical metals content are extremely low and below the detection limit of the analytical apparatus (Abreu *et al*., 2007). Although the abandoned mine impact on the surface waters be confined to the mining area, further studies are needed to understand the impact on groundwaters. In fact, some of the region groundwaters present total arsenic concentrations higher than 50 µg L^{-1} (Matias *et al*., 2006) which is five times higher than the allowed concentration for human consumption, according to the Portuguese and European laws.

A soil survey undertaken in approximately one square kilometre inside the mine area showed that the most contaminated zones were located: near the old mine infrastructures; in the tailings neighbourhood, where soils located down the slope were impacted by wind and water erosion (occurring deposits and element enrichment); and on soils developed on waste materials where vegetation was already growing. Arsenic is the most important contaminant of these soils where concentrations are above the maximum allowed values for soils according to the CCME legislation (1997) (Table 5). Soils are acidic with pH ranging between 2.91 and 5.46. The soil organic carbon content is quite variable (48.2 ± 43.4 g kg^{-1}) (Abreu *et al*., 2007).

Table 5. Statistics of concentrations of chemical elements in soils (DW) from Penedono mine area

	Al	As	Cu	Fe	Mn	Pb	S	W	Zn
	g kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}	g kg^{-1}	mg kg^{-1}	mg kg^{-1}
Geom. mean	32.7	2558	88.1	26.5	198.0	89.9	0.760	50.6	88.4
Minimum	3.4	88	13.7	10.4	65.6	33.6	0.145	6.0	28.7
Maximum	60.4	34000	592.9	481	570.4	1121.7	15.9	656	605.6
MAV*	–	12	63	–	–	70–140	–	–	200

*MAV: maximum allowed values for soils according to CCME (1997) for agriculture and residential use; DW – dry weight

Figure 4. Penedono mine area — Waste dumps more intensely colonized by *Pinus pinaster*, *Quercus pyrenaica*, *Cytisus* spp. and *Poaceae* grasses

In the least contaminated sites, the mine area presents a relatively good vegetation cover, which consists mainly of small woods of pines and chestnut trees explored by local farmers, grass for cattle grazing as well as some spontaneous shrubs. In the more contaminated areas a natural visual attenuation occurs (Figs. 3 and 4). Anyhow, several plant species are growing spontaneously or have been planted in those areas. Growing on the dumps or on the contaminated adjacent soils were found: three trees species – pine trees (*Pinus pinaster* Aiton), chestnut trees (*Castanea sativa* Mill.), and oak trees (*Quercus pyrenaica* Willd.); four spontaneous shrubs – *Cytisus multiflorus* (L'Hér.) Sweet, *Cytisus striatus* (Hill.) Rothm, *Echinospartum ibericum* Rivas Mart., Sánchez Mata & Sancho, and *Erica lusitanica* Rudolphi; and two grass species – *Arrhenatherum album* (Vahl) W. D. Clayton and *Deschampsia caespitosa* (L.) P. Beauv..

Trees, in general, showed a good vegetative development. In some few soils, highly contaminated with arsenic and/or with high content of available aluminium some colonizing trees, especially pines and chestnuts, showed yellowish leaves and are shorter than the other trees. Shrubs as *E. ibericum*, *C. multiflorus* and *C. striatus* showed good growth rate and present an excellent soil cover capacity especially the last two species that can attain 2 – 3 m hight. Regarding the uptake of hazardous chemical elements, the soil – plant chemical elements transfer (TC) is <1 for almost all the analysed elements, with exception for manganese where $TC_{Mn} > 1$ for all the plant species. The TC values show that the plant species are not aluminium, arsenic, copper, lead, tungsten, and zinc accumulators. Arsenic concentration in shoots and leaves have the highest value (268 mg kg^{-1} DW) in *C. multiflorus* (geom. mean 14.4 mg kg^{-1} DW). *Pinus pinaster* (geom. mean 32.8 mg kg^{-1} DW) and *C. striatus* (geom. mean 25.4 mg kg^{-1} DW) globally have higher values for arsenic concentrations than *C. multiflorus*, as can be seen from their geometric means, but as individuals they have lower maximum values (150 and 248 mg kg^{-1} DW, respectively). These plants are extremely tolerant to arsenic as their content, for most of the plants, exceeded the values considered toxic for the majority of the plants (5 – 20 mg As kg^{-1}; Kabata Pendias & Pendias, 2001). Despite of the lead concentration in some soils and waste materials the plants showed relatively low levels of the element (ranging between 0.004 and 2.62 mg kg^{-1} DW) which is below the concentrations considered sufficient or normal for various species (5 – 10 mg Pb kg^{-1}; Kabata Pendias & Pendias, 2001). The concentration of tungsten in plants was also low, but exceeds, for some samples, and particularly for *Cytisus* (1.5 – 5.6 mg kg^{-1} DW) plants the reference value (0.2 mg W kg^{-1} DW). *Castanea sativa* and its nuts as well as *Q. pyrenaica* contained low levels of hazardous chemical elements, but aluminium can attain in the first species concentrations (117 – 1930 mg kg^{-1} DW) above the considered normal for plants (50 to 200 mg Al kg^{-1}; Srivastava & Gupta, 1996). Also *P. pinaster*, *C. multiflorus* and *E. lusitanica* showed high aluminium content in the aboveground parts of the plant without toxicity symptoms, except for some few pine trees. The grass species also seem to be arsenic tolerant and the translocation of the element to the aerial part of the plant is not elevated (geom. mean 16.2 mg kg^{-1} DW) and do not represent hazard for cattle or wildlife.

The native and/or spontaneous plants growing on the mining area of Santo António are completely adapted to the contaminated environment and seem to reveal a high remediation potential, both by physical and chemical stabilization of waste materials and contaminated soils. A program of phytostabilization can be easily accomplished especially by means of shrubs (*C. multiflorus, C. striatus* and *E. ibericum*) and *Pinus* plants. These plants have high soil coverage capacity and biomass production and are tolerant to high soil arsenic concentrations. However, studies on surface and underground water monitoring must be undertaken.

Braçal Mine

The Braçal lead mine is located to the northeast of Aveiro, some 40 km southeast of Porto, in the Central Iberian Zone (Fig. 1). This mine was already mined for lead, in roman times, as has been testified by several artefacts (Cerveira, 1966), and in modern times have been worked between 1836 and 1958. Besides lead extraction, concentrated ore was also produced, and the structures that had supported mineral separation, and metallurgic work, are still present in the area. Galena was the principal sulphide mineral exploited as source of lead, but pyrite, calcite and other carbonates (Fonseca *et al.*, 1986) can also be found.

Waste dumps containing coarse slags constitute the main tailings. Fine sandy materials are also identified in the area. These waste materials still contain high levels of lead, zinc and iron. During the last 50 years, a thin layer of soil was developed on waste materials and/or host weathered rocks (a complex of shales and greywackes from ante-Ordovician age), where a variety of plants are growing.

Among the plants growing in the area, the following species were identified: shrub plants – *Calluna vulgaris* (L.) Hull, *Cistus inflatus* Pourr. ex Demoly, *Erica arborea* L. and *Ulex minor* Roth, and trees – *Acacia dealbata* Link, *Acacia melanoxilon* R. Br., *Eucalyptus* *globulus* Labill, *Pinus pinaster* Aiton, and *Quercus robur* L.. All the shrubs are native plants growing spontaneously in the region, but *Eucalyptus*, *Pinus* and *Quercus* were planted (Fig. 5). *Eucalyptus* has been planted as raw material to the pulp and paper industry. All the plants are well developed without any sign of phytotoxicity (Anjos *et al.*, in preparation).

a **b**

Figure 5. (a) Waste dumps containing coarse slags where mainly *Acacia* trees are growing. (b) Fine waste materials colonized by *Cistus inflatus*, *Erica arborea*, *Quercus robur*, *Acacia* spp, etc.

Soils from the mining area present pH between 4.9 and 7.7 (median 5.4) and contain high levels of total lead, which are above the maximum allowed values for soils according to the CCME legislation (1997), as can be seen from Table 6. Some soils also contain copper and zinc concentrations slightly higher than the established by the Canadian legislation (CCME, 1997) for agriculture and/or residential use.

Table 6. Statistics of concentrations (mg kg^{-1} DW) of trace elements in soils from Braçal mining area (Anjos *et al.*, in preparation)

	Pb	Mn	Cu	Zn	Cd
Median	5250	207	109	314	1.8
Minimum	1480	124	32	62	0.8
Maximum	13400	499	712	905	6.1
MAV*	70–140	–	63	200	1.4–10

*MAV: maximum allowed values for soils according to CCME (1997) for agriculture and residential use; DW – dry weight

Plants growing in Braçal mining area are not lead accumulators, but *C. inflatus* species can be classified as manganese and zinc accumulator (Anjos *et al.*, in preparation) as TC > 1 for these elements. Besides this accumulator behaviour for specific chemical elements, the concentrations attained in the aboveground part of the plant (median values (DW): 107 mg Mn kg^{-1}; 173 mg Zn kg^{-1}) are not enough high for being considered as hyperaccumulators or to represent a health risk for livestock or wildlife, and can be used for phytostabilization purposes. Most of the plants collected in Braçal mine area revealed metal concentration within the normal range for generalized plant species (Kabata-Pendias & Pendias, 2001), and below the maximum tolerable levels for cattle (Mendez & Maier, 2008b). There were, however, some exceptions for lead, which attain concentrations above the toxicity limits for plants in *C. inflatus* (49.5 – 217 mg kg^{-1} DW) and some few plants of *E. arborea* (23.8 – 140 mg kg^{-1}DW), and *U. minor* (9.2 – 70.8 mg kg^{-1} DW), moreover do not presenting any visible signs of toxicity. Trees, particularly those who can be used for economic purposes (*Eucalyptus globulus* and *Pinus pinaster*) showed a good vegetative development and metal concentration within the normal or sufficient range for vegetation; lead in these species ranged between 4.7 and 44.4 mg kg^{-1} DW, but *P. pinaster* presented the lowest median value (8.7 mg kg^{-1} DW).

Sediments collected in the river Mau, which drains the mine area, showed high levels of trace elements, especially lead and cadmium, and to some extent zinc, reflecting the past mining activities (Nunes *et al*., 2003). Besides the contaminated sediments and also the high concentrations of lead in soils, as well as other chemical elements, the water of river Mau has a good chemical quality: pH ≈ 7, conductivity ≈ 0.068 mS cm^{-1}, and trace elements concentration below the detection limits (Nunes *et al*., 2003).

In the Braçal mine area trees together with shrubs are a good combination for phytostabilization, particularly for mining wastes stabilization. The deep well developed root system of the trees that penetrate in depth makes possible a hydraulic control, while the shrubs create a vegetative surface cap preventing air and water erosion, and probably chemical elements leaching.

Panasqueira Mine

Still in operation tungsten Panasqueira mine is located in the Central Iberian Zone to the northwest of Castelo Branco, about 35 km from Fundão and some 200 km from Porto city (Fig. 1). Historical data shows that Romans worked the area for tin. The first wolframite mineralization in the area was reported in 1888 and the mine has been operating more or less continuously from 1896 until now except for a brief period at the end of the World War II and a second closure in the mid 1990's. The present Panasqueira concessions of Beralt Tin & Wolfram Company occupy an area around 20 km^2. From 1947 to 2001, was mined around 26 Tg of rock, from where about 92.8 Gg of tungsten, 4.8 Gg of tin and 28.6 Gg of copper concentrates were obtained (Cavey & Gunning, 2006; Smith, 2006).

The Panasqueira ore deposit, one of the largest economic vein deposits in the world, is a typical example of a tin – tungsten hydrothermal mineralization associated with the hercynian plutonism. It consists of a series of stacked, sub-horizontal, hydrothermal quartz veins intruding into the Beira-Schist Formation containing mainly wolframite, arsenopyrite, pyrite, chalcopyrite and cassiterite. The mineralized zone has dimensions of approximately 2.5 km in length; it varies in width from 400 to 2200 m and continues to at least 500 m in depth (Cavey & Gunning, 2006; Corrêa *et al.*, 1999; Noronha *et al.*, 1992; Thadeu, 1951). Wolframite mineralization occurs as very large crystals or large crystals aggregates usually concentrated towards the margins of the quartz veins or, occasionally, close to the central portion of the quartz veins. Spectacular crystals, filling open spaces and vugs, are frequently observed in the quartz veins (Corrêa *et al.*, 1999). Minerals as wolframite and apatite from Panasqueira are world renowned, and arsenopyrite, cassiterite, siderite and quartz are famous due to its dimension and quality. Panasqueira is a known georeferenced site for minerals/crystals collectors. At Panasqueira deposit, more than 64 minerals, including arsenates, carbonates, oxides, phosphates, silicates, sulphides and sulphosalts, and tungstates, have been identified (Kelly & Rye, 1979; Corrêa *et al.*, 1999).

The Panasqueira area includes three subareas: Cabeço do Peão, Panasqueira and Barroca Grande. Cabeço do Peão, nowadays inactivated, was the first site where the wolframite ore, from different Panasqueira mining sites, was recovered from 1904 to 1996, when the last concentration equipment was removed to the present location in Barroca Grande. In 1912 the mining company installed an aerial 5100 m rope-tramway that brought the ore from different mining sites at Panasqueira to the Cabeço do Peão plant (Corrêa *et al.*, 1999). This abandoned sub-area, located near the river Zêzere comprises several facilities and large wasted heaps (approximately 1 200 000 m^3) located downslope from the old plant. These tailings with an average height of 90 m and high slopes (> 70%) have been disposed for about 90 years. They represent a potential massive failure danger (e-EcoRisk project: http://www.e-ecorisk.info/) together with a chemical danger rising from generated acid mine draining directly into the river Zêzere, and mechanical dispersion of hazardous chemical elements (Ávila *et al*., 2008). This river is one of the most important Portuguese rivers and the main source of water for the city of Lisboa. In spite of the existence of tourist and educational plans for Cabeço do Peão site, to be implemented by the municipalities, the unique recovery measures, undertaken until 2008, were related with the capping (June 2006) with geotextile and layers of clay of an arsenopyrite stockpile (9 400 m^3) (Ávila *et al*., 2008). A sparsely vegetation composed mainly by *Pinus* spp. together with some shrubs as *Erica* spp, and *Cistus* spp were observed in some places of the waste dumps (Fig. 6).

Figure 6. Panasqueira mine — Cabeço do Peão subarea showing old waste dumps near the river Zêzere.

Panasqueira subarea contains the old mine that ceased its activity in 1965, remnants of old buildings, large tailing piles downslope from the old mill building as well as several small waste dumps scattered around the hillside. Waste materials are naturally revegetated (sparsely or even more dense in some places (Fig. 7)) by pine trees (*Pinus* spp), by grasses and shrubs belonging mainly to the families *Poaceae* (*Agrostis* spp.), *Cistaceae* (genus *Cistus*), *Ericaceae* (genera *Erica* and *Calluna*) and *Leguminosae* (genera *Cytisus* and *Ulex*). However, there are no studies for assessing the environmental risks in this site. A complete review of the potential environmental problems at the old Panasqueira site is needed as well as a biogeochemical study addressed to the spontaneous plant species growing in the area.

Figure 7. Panasqueira mine – Waste dumps from Panasqueira subarea well colonized by native (*Erica* spp., *Calluna vulgaris*, *Cytisus* spp, *Ulex* spp., etc.) and introduced (*Pinus* trees) vegetationn.

Barroca Grande subarea includes the present underground mine processing plant and portals, mine offices, old and recent dumps as well as active tailings disposal areas, and a water treatment plant built in 1957 at Salgueira and located 1 000 m downstream from the main mining operations. The main environmental concerns for this site are related to the active waste dumps (Fig. 8) and the Salgueira water treatment plant.

Figure 8. Panasqueira mine – active and bared waste dumps, old waste dumps vegetated with *Pinus pinaster* and *Arbutus unedo*, together with shrubs, and the water treatement plant at Barroca Grande subarea.

Table 7. Minimum and maximum concentrations of chemical elements in waste materials (mg kg^{-1} DW) from Barroca Grande (Panasqueira mine) (adapted from Ávila *et al.*, 2008; Godinho, 2008)

	As	Cd	Cu	Pb	Sb	Sn	W	Zn
Minimum	466	2.6	214	29	29	453	40	340
Maximum	12000	87	3741	282	118	882	12000	4224

DW – dry weight

The waste heaps, growing every day, extend along more than one kilometre southeast from the mine portals and along the north river side of the small creek named Ribeira do Bodelhão that flows south-easterly to the Rio Zêzere. These dumps composed of gravel, stones and sand materials present steep slopes and are bared (Fig. 8). The wastes contain high concentrations of several hazardous chemical elements (Table 7).

The Salgueira water treatment plant with a capacity of 300 m^3/h receives the discharge of underground mine water via a drainage tunnel, water from two pond areas and seepage water from the base of the tailings. However, the mine water flows are seasonal, ranging approximately from 250 m^3/h during the summer to 600 m^3/h during the winter. As a result, during the winter not all the water can be treated and is discharged directly to the Ribeira do Bodelhão. High concentrations of hazardous chemical elements were found in the water and in the sediments of this creek collected downstream from Salgueira plant to the creek mouth (Table 8; Ávila *et al*., 2008; Godinho, 2008; Faria *et al*., 2008). The main water discharge point showed typical pH of acid mine drainage water and the concentration for arsenic, copper, manganese and zinc exceeded the regulatory limits for water quality both for drinking and irrigation (Cavey & Gunning, 2006). In the Salgueira plant the water is treated with lime and the precipitated sludge (fine material) is pumped into the tailings pond (active dam) which represents another point of environmental concern, as the two ponds (old and active dam) are deficiently impermeable. Samples of dam materials collected by Ávila *et al*. (2008) showed high concentrations of hazardous chemical elements (Table 9).

Table 8. Statistics of concentrations of chemical elements in sediments (mg kg^{-1} DW) and water (mg L^{-1}) in the Ribeira do Bodelhão collected from Barroca Grande site to the mouth (Panasqueira mine)

	As	Cd	Cu	Fe	Pb	S	W	Zn
Sediments								
Median[(a)]	732	19.5	1115	45500	31	nd	318	1004
Minimum[(a)]	91	2.0	116	36000	19	nd	101	240
Maximum[(a)]	18000	268	4561	81000	117	nd	4103	3562
Geometric mean[(b)]	17857	24.8	3758	89563	206	18582	2187	2433
Minimum[(b)]	5560	11.4	1990	59200	95	7200	1040	1290
Maximum[(b)]	44000	138	6860	122000	423	66900	6320	14100
Geometric mean[(c)]	89.3	0.20	21.7	563	1.13	nd	nd	19.1
Minimum[(c)]	25.8	0.10	15.8	417	0.43	nd	nd	12.8
Maximum[(c)]	150	0.29	29.9	718	1.68	nd	nd	22.7
Water								
Minimum[(a)]	5	15	190	100	< 22	152[(d)]	nd	2000
Maximum[(a)]	13	58	600	290	< 22	605[(d)]	nd	6300
Geometric mean[(c)]	0.08	0.03	0.32	0.33	< dl	nd	nd	3.60
Minimum[(c)]	0.03	0.01	0.08	0.05	< dl	nd	nd	1.94
Maximum[(c)]	0.5	0.1	1.02	0.99	< dl	nd	nd	9.29

Adapted from [(a)]Ávila *et al.*, 2008, [(b)]Godinho, 2008, [(c)]Faria *et al.*, 2008; dl: detection limit; nd: not determined; [(d)]: SO_4^{2-}; DW – dry weight

Table 9. Minimum and maximum concentrations of chemical elements in dam materials ($mg\ kg^{-1}$ DW) from Barroca Grande (Panasqueira mine) (adapted from Ávila *et al.*, 2008)

	As	Cd	Cu	Pb	Sb	Sn	W	Zn
Minimum	2715	41	1755	28	12	147	1590	433
Maximum	200000	1813	9800	934	150	1643	10300	7300

DW – dry weight

Although both dams (old and active) had similar ranges for the concentrations of the majority of the trace elements, the old one may pose a more considerable potential threat as a consequence of being located closer to Ribeira do Bodelhão and of containing finer particle size materials (Ávila *et al.*, 2008).

The stabilization of some old tailings (60 – 80 years old) in Barroca Grande subarea was already accomplished by nature. This fact seems to indicate the possible success of a phytostabilization program in the area. These dumps show the development of a thin layer of soil and present an effective vegetation cover mainly composed of *Arbutus unedo* L., *Calluna vulgaris* (L.) Hull, *Cistus ladanifer* L., *Cytisus striatus* (Hill.) Rothm, *Erica arborea* L., *Erica australis* L., *Pinus pinater* Aiton and *Ulex* spp.. The soils that receive the drainage influence of the recent waste dumps also present a well-adapted vegetation cover besides the high concentrations of some hazardous chemical elements. The studies on soils and *Arbutus unedo*, a plant species whose fruits are used for firewater production called "aguardente de medronho", showed: hazardous chemical elements concentrations, in many soil samples, above the allowed values (Table 10); and low trace elements concentrations in the aboveground part of *A. unedo*, including the fruits, lying within the normal range for various plant species (Godinho, 2008; Godinho *et al.*, 2009). However, 20 % of the *Arbutus unedo* samples (branches and leaves only) contained cadmium concentrations above the normal range for mature leaf tissues for various species lying within the excessive or toxic range (5 – 30 $mg\ kg^{-1}$, Kabata-Pendias & Pedias, 2001), although no visual symptoms of toxicity were observed.

Table 10. Statistics of concentrations of chemical elements in soils and *Arbutus unedo* ($mg\ kg^{-1}$ DW) in Panasqueira mine (Godinho, 2008)

	As	Cd	Cu	Pb	S	Sb	W	Zn
Soil								
Geometric mean	680	2.37	233	60	618	2.2	138	332
Minimum	158	0.6	51	28	200	0.2	19	142
Maximum	7790	79	4080	205	6000	32.1	1450	12300
Arbutus unedo								
Geometric mean	1.4	1.04	3.5	0.41	nd	< 0.1	0.49	100
Minimum	< dl	0.26	2.1	0.2	nd	< 0.1	< dl	26
Maximum	5	12.9	12.9	1.3	nd	< 0.1	3.4	570

dl: detection limit; nd: not detected; DW – dry weight

The calculated soil–plant transfer coefficient (TC) for all the hazardous chemical elements is <1 except for cadmium in the referred very few samples. The hazardous chemical elements non-accumulator characteristics, together with a luxuriant vegetative development and economical value (firewater production) indicate *Arbutus unedo*, in association with other species also well established in the contaminated areas, for phytostabilization programs at the Panasqueira mine area as well as other sites with similar edaphoclimatic characteristics.

The recent bared dumps (Fig. 8) should be embanked in platforms in order to decrease slope, and an environmental rehabilitation plan should be improved. This plan must include an assisted revegetation using adequate amendments and local tolerant plant species already identified and growing spontaneously on the oldest waste materials. *Pinus pinaster* trees and *Arbutus unedo* shrub should be used with an economic profit.

South of the River Tejo Mining Sites

Aljustrel Mine

Aljustrel mining site, with an area of approximately 14 km^2, is located in the Alentejo province south of Portugal, some 150 km southeast from Lisboa and 30 km southwest from Beja (Fig. 1). This mine centre, exploited during Roman era in gossan and supergene zones until 100 m deep, is one of the biggest Iberian Pyrite Belt mining sites. The Iberian Pyrite Belt is a world-class volcanic-hosted massive sulphides metallogenic province (Barriga *et al.*, 1997; Oliveira *et al.*, 2006; Silva *et al.*, 1997; Tornos, 2006). The modern exploitation of the Aljustrel mine was developed from 1850 to 1993, when the activity was suspended, entering in stand by maintenance, till 2007 when the mine was reopen for zinc extraction.

In the Aljustrel mine area are recognised six polymetallic massive sulphide (copper, lead, zinc) orebodies: Algares, São João, Moinho, Feitais, Estação and Gavião (Matos *et al.*, 2003; Matos & Martins, 2006; Silva *et al.*, 1997). The environmental impacts related with mining activities are mainly due to: the presence of some unsafe and dangerous mining infrastructures, like open pits, galleries and mining shafts exposed in the local urban areas (Aljustrel village); significant geotechnical instability at São João open pit walls and Malpique and Moinho quarries; decantation lakes, mining dams and associated channel system containing acid waters rich in trace elements; waste tailings (> 3 Mt) composed of Roman slag, pyrite ore (blocks and brittle massive pyrite ore) and host rocks, that occupy large areas and presenting, in some cases, high volume heaps that are submitted to strong erosion processes (Matos *et al*., 2003; Luís *et al*., 2008).

The waste materials, containing mainly arsenopyrite, chalcopyrite, copiapite, galena, marcasite, natrojarosite, pyrite, schwertmannite, siderotil, and sphalerite, generate acid mine drainage (Bobos *et al.*, 2006; Luís *et al*., 2008), which is mainly drained to the Água Forte stream. The tailings present high concentrations of several hazardous chemical elements as arsenic, cadmium, cobalt, copper, lead, mercury, molybdenum, strontium and zinc, as well as gold and silver (Luís *et al*., 2008; Matos *et al.*, 2003). Chemical analysis, done by Bobos *et al*. (2006) in mill tailings from Algares, showed high concentrations of arsenic and hazardous metals (Table 11).

Table 11. Minimum and maximum concentrations of chemical elements in mill tailings (mg kg^{-1} DW) from Algares (Aljustrel mine) (adapted from Bobos *et al.*, 2006)

	As	Co	Cu	Pb	Sn	Zn
Minimum	146	97	173	122	<5	336
Maximum	1618	157	1073	10955	219	8001

DW – dry weight

As a consequence surface waters, specially those from de Água Forte stream, presented low pH values (1.5 to 3.5) and high arsenic and metal concentrations: arsenic (6.84 mg L^{-1}); cadmium (0.455 mg L^{-1}); copper (68.8 mg L^{-1}); iron (1262 mg L^{-1}); lead (0.136 µg L^{-1}); manganese (19.5 mg L^{-1}); and zinc (264.4 mg L^{-1}) (Luís *et al*., 2008).

Table 12. Statistics of concentrations of chemical elements in sediments (mg kg^{-1} DW) from Água Forte stream, Aljustrel mine (adapted from Luís *et al*., 2008)

	As	Cd	Cu	Fe	Mn	Pb	Sb	Zn
Geometric mean	929	0.6	445	117403	419	730	63	368
Minimum	168	0.2	280	48600	155	260	17	216
Maximum	2490	2.6	843	213300	991	2627	311	937

DW – dry weight

Stream sediments, of the same watercourse, also analysed by Luís *et al*. (2008) showed high chemical elements concentrations (Table 12) that exceeded criteria for benthic organisms. In fact, in these contaminated sites a decrease of diversity in diatom communities, elimination of sensitive taxa and shifts in taxonomic composition were observed, when compared with the diatom communities from sites moderately to low influenced by acid mine drainage in the same studied area (Luís *et al*., 2008).

Table 13. Statistics of concentrations of chemical elements in soils (mg kg^{-1} DW) in Aljustrel mine (adapted from Alvarenga *et al.*, 2004; 2008a; Pereira, 2005)

	As	Cu	Mn	Pb	Zn
Alvarenga *et al*., 2004					
Geometric mean	269	453	344	691	327
Minimum	45	164	75	215	140
Maximum	565	1800	1200	3500	945
Pereira, 2005					
Geometric mean	~	951	747	2258	483
Minimum	~	60	249	931	274
Maximum	~	4345	1839	5482	1045
Alvarenga *et al*., 2008a	~	362	~	1250	245

DW – dry weight

A preliminary soil survey executed by the Portuguese Geological Survey (Laboratório Nacional de Energia e Geologia – LNEG, former IGM) (Matos & Rosa, 2001) in Aljustrel mine indicated a soil contamination by arsenic, barium, cadmium, lead, mercury and zinc. More specific studies were undertaken on soils in the Algares site, where the orebody was exploited since Roman times, and where the environmental impacts generated by the exploitation are more visible. Soils presented high concentration of arsenic, copper, lead, manganese, and zinc (Table 13). Cadmium, chromium and nickel were also analysed in one soil sample by Alvarenga *et al.* (2008a), showing the concentrations of: 2.6, 21.8 and 15.4 mg kg^{-1}, respectively.

Table 14. Statistics of concentrations of chemical elements in plants (mg kg^{-1} DW) from Aljustrel mine (adapted from Alvarenga *et al.*, 2004; Fernandes & Henriques, 1989; and Pereira, 2005)

	Cu	Mn	Pb	Zn
Cistus ladanifer[(a)]				
Geometric mean	14.8	532	11.8	222
Minimum	8.3	117	2.0	99
Maximum	29.7	1399	33.0	583
Spergularia fasciculata[(b)]	19.5	103	28.6	59.8
Rumex bucephalophorus[(b)]	69.2	168	64.1	129.3
Pteridium aquilinum[(b)]	9.4	209	32.3	23.2
Chaetopogon fasciculatus[(b)]	611	530	15.3	173
Jasione montana[(b)]	98.8	188	15.8	189.6
Quercus rotundifolia (leaves)[(c)]	324	1844	323	451
Quercus rotundifolia (fruits)[(c)]	37	291	20.5	58.5

[(a)]Alvarenga *et al.*, 2004; [(b)]Pereira, 2005; [(c)]Fernandes & Henriques, 1989; DW – dry weight

Several plants growing in contaminated soils of the Aljustrel mine area were identified: *Chaetopogon fasciculatus* L., *Cistus ladanifer* L., *Cistus monspeliensis* L., *Cistus crispus* L., *Cistus salviifolius* L., *Genista hirsuta* Vahl, *Jasione montana* L., *Lavandula luisieri* (Rozeira) Rivas-Martinez, *Pteridium aquilinum* (L.) Kuhn, *Quercus rotundifolia* Lam., *Rumex bucephalophorus* L., and *Spergularia fasciculata* L.. Some of these species, all collected in the Algares site, were studied to evaluate their potential for phytostabilization (Table 14) (Alvarenga *et al*., 2004; Fernandes & Henriques, 1989; Pereira, 2005).

The plants are not metal accumulators as the transference coefficient for metals is <1 and its concentration in the plant shoots is below the tolerable limit for animal toxicity. *Quercus rotundifolia* is an exception for lead, as its leaves contained 323 mg Pb kg^{-1} (three times more than the limit allowed for cattle, according to Mendez & Maier, 2008b), but the element is not strongly translocated to the fruits (20.5 mg Pb kg^{-1}) which are the part of the plant eaten by animals. The characteristics of these spontaneous plants and their adaptation to the physic, chemical and climatic conditions of the area make these species worth considering for phytostabilization programs in this mine site.

Greenhouse pot experiments were conducted by Alvarenga *et al*. (2008b; 2008c) to evaluate the effect of different soil amendments in the remediation of a soil from Aljustrel (Algares site) with pH between 3.4 – 3.8 and heavy metals content (mg kg^{-1}) as follows: Cd 2.6 ± 0.2; Cr: 21.8 ± 0.6; Cu: 362 ± 23; Ni: 15.4 ± 0.4; Pb: 4350 ± 169; Zn: 245 ± 64. Sewage sludge from a municipal waste water treatment plant, compost from organic fraction of unsorted municipal solid waste, garden waste compost alone or in combination with liming materials, as sugar beet sludge, agriculture limestone, and calcium oxide, were used as soil correctors. The application of composts and liming materials was effective in soil remediation for copper, lead and zinc once their biovailable fraction decreased. Soil ecotoxicity (with and without soil amendments) was directly evaluated in plants and also in soil leachates using indirect exposure bioassays (luminescent inhibition of *Vibrio fischeri* and *Daphnia magna* immobilization). In general, sewage sludge (SS) and sugar beet sludge suppress soil toxicity, but high application rate (200 Mg ha^{-1}) of SS was toxic to plants and *V. fischeri* (Alvarenga *et al*., 2008c).

The use of a perennial ryegrass (*Lolium perenne* L.) together with the above mentioned soil amendments for the Aljustrel soil phytostabilization was also evaluated (Alvarenga *et al*., 2008b). Soil treatments did not significantly reduce copper, lead and zinc uptake by the plant although the plant biomass was increased. Those authors concluded that the municipal solid waste compost (50 Mg ha^{-1}) can be used successfully in that soil remediation by correcting soil acidity, and increasing soil organic matter and nutrients supply (nitrogen, phosphorus and potassium) allowing the establishment of perennial ryegrass. However, once the lead content in the plant shoots (154 – 295 mg kg^{-1}, Alvarenga *et al*., 2008b) is above the limit for the domestic animal toxicity (100 mg kg^{-1}, Mendez & Maier, 2008b), this plant species should be used carefully.

The use of spontaneous and well adapted plant species growing in the contaminated soils of the Aljustrel area, together with biologically reactive organic matrices as those studied by Alvarenga *et al*. (2008b; 2008c; 2008d) should be considered to the phytostabilization of this mine area. Moreover, as the ore mined in Aljustrel also contain arsenopyrite, the arsenic behaviour in soil and plants must also be studied as it is frequently different from metals behaviour in the presence of soil amendments.

Neves Corvo Mining Area

The Neves Corvo mining area, located in the Baixo Alentejo region, some 55 km SSW from Beja (Fig. 1), includes the “Mina de Neves Corvo”, that started exploitation in 1988 for copper and tin and six abandoned mines: Brancanes (closed by the end of the XIX century), mined for copper in chalcopyrite and Cerro do Algaré mined for pyrite and copper in chalcopyrite and arsenopyrite; the other four mines (Courela das Ferrarias (closed in 1987), Herdade do Castelo, Cerro da Cachaçuda, and Cerro das Guaritas) were all mined for manganese in pyrolusite primary minerals (Batista, 2003; Batista *et al*., 2007). The “Mina de Neves Corvo”, located in the Iberian Pyrite Belt, is one of the few copper and tin mines still operating in Europe, and is considered as one of the most important copper deposits in the world. The mine also has large reserves in zinc. The “Mina de Neves Corvo” contains more than 300 Tg of massive sulphides separated into five orebodies: Corvo, Graça, Neves, Lombador and Zambujal, but only the first three are nowadays in exploitation. There are three main types of mineralization at “Mina de Neves Corvo”: massive sulphides (the more abundant), with cupriferous ores, cupro-stanniferous, zinc-rich ores, and complex ores (copper-lead-zinc ores); fissural or stockwork mineralization, with cupriferous, stanniferous and zinc ores; and *rubané* (banded or veining ores), with copper and tin (Moura, 2008). The “Mina de Neves Corvo” deposit can be distinguished from the other massive sulphide deposits of the Iberian Pyrite Belt and worlwide by the high-grade copper ores (large volumes with more than 20% copper, mainly in chalcopyrite and tennantite-tetrahedrite), and the abundance and grades of the tin ores, locally with metric-scale blocks of almost pure cassiterite (up to 65% tin) (Moura, 2008).

The exploitation, in the mining area, was inconstant from the XIX century when Brancanes Mine began until actuality in “Mina de Neves Corvo”. In the “Mina de Neves Corvo” the exploitation was only possible due to geophysical techniques of prospecting. The ores are very deep and consequently not possible to discover with the old exploration methods. In fact, there are no records of ancient exploitations in the “Mina de Neves Corvo”.

A soil survey in the Neves Corvo mine area, including the “Mina de Neves Corvo”, the six abandoned mines (five located at the northwestern part of the Neves Corvo (Courela das Ferrarias, Herdade do Castelo, Cerro da Cachaçuda, Cerro das Guaritas and Cerro do Algaré) and Brancanes located in the southwestern part), and the soils located over the deep and unexploited orebody of Lombador were done by Batista (2003) and Batista *et al*. (2007), ten years after the mining started in the “Mina de Neves Corvo” (Table 15). Results on soils from the “Mina de Neves Corvo” were also obtained by Farago *et al*. (1992) one year after the Neves Corvo mine opening (Table 15). Comparing the results obtained in both campaigns (soil sampling in 1989 by Farago *et al*. (1992) and in 1998 by Batista *et al*. (2007)) it is evident the increase on copper, lead and zinc concentrations as a consequence of 10 years of mining. Soil pH showed a slightly decrease for the same area from 4.1-7.1 (Farago *et al*., 1992) to 3.45-5.69 (Batista *et al*., 2007).

Table 15. Concentrations range (minimum-maximum) of chemical elements in soils (mg kg^{-1}DW) in Neves Corvo mining area (adapted from Batista *et al.*, 2007; Farago *et al.*, 1992)

	Cu	Fe	Mn	Pb	Zn
“Mina de Neves Corvo”[(a)]	179–6138	23800–47600	403–3195	23–175	78–607
Brancanes old mine[(a)]	28–62	28500–34400	495–1524	12–38	32–59
*Northwestern area[(a)]	32–361	18500–39800	1158–4060	38–139	28–286
**Lombador[(a)]	15–20	21100–22600	411–543	10–14	32–42
“Mina de Neves Corvo”[(b)]	15–255	–	–	9.9–34.7	33.4–118

*abandoned mines (Courela das Ferrarias, Herdade do Castelo, Cerro da Cachaçuda, Cerro das Guaritas and Cerro do Algaré) located northwestern of “Mina de Neves Corvo”; **soils collected over a deep and unexploited orebody;[(a)] Batista *et al*., 2007; [(b)] Farago *et al*., 1992. DW – dry weight.

Cistus bushes, especially *Cistus ladanifer* L., are the best distributed plant in the region, but other species were also identified: *Quercus rotundifolia* Lam. and *Quercus suber* L., as trees; and other bushes, as for example, *Cistus monspeliensis* L., *Cistus salviifolius* L., *Cistus crispus* L., *Salvia lavandulifolia* Vahl, *Lavandula stoechas* L., *Rosmarinus officinalis* L., *Thymus vulgaris* L., etc. (Richards, 1995). The concentrations of copper, iron, manganese, lead and zinc in *Cistus ladanifer* plants collected in the mine area are presented in Table 16.

Cistus ladanifer seems to have an adaptation mechanism to the different copper concentrations in soils. This plant species is better adapted to areas where copper concentrations are much above the toxicity limits to plants than for copper concentrations below the limit of deficiency to plants in soils (Batista *et al*., 2003). Tin, exploited in the

"Mina de Neves Corvo", showed in soils concentrations ranging from 1 to 178 mg kg^{-1} being the highest values found near the mine facilities. There is a positive correlation between tin in soil and *C. ladanifer* both in shoots (maximum 15.7 mg kg^{-1} dry weight) and roots (maximum 62.7 mg kg^{-1} dry weight) (Batista *et al.*, 2008).

Table 16. Concentrations range (minimum-maximum) of chemical elements in the aboveground part of *Cistus ladanifer* L. (mg kg^{-1} DW) in Neves Corvo mining area (adapted from Batista *et al.*, 2007; Farago *et al.*, 1992)

	Cu	Fe	Mn	Pb	Zn
"Mina de Neves Corvo"[(a)]	64.4–591.5	579–4648	213–1233	2.4–24.1	54.4–177
Brancanes old mine[(a)]	7.1–10.9	351–969	558–1212	0.6–0.8	12–19.8
*Northwestern area[(a)]	22.6–98	313–1800	445–1171	1.1–4.5	60.4–155
**Lombador[(a)]	8.9–10.1	593–669	511–1056	0.8–0.9	39.6–63.4
"Mina de Neves Corvo"[(b)]	30.3–91.2	–	–	3.3–11.1	26.1–54.2

*abandoned mines (Courela das Ferrarias, Herdade do Castelo, Cerro da Cachaçuda, Cerro das Guaritas and Cerro do Algaré) located northewesten of Neves Corvo mine; **plants growing in soils collected over a deep and unexploited orebody; [(a)]Batista *et al.*, 2007; [(b)]Farago *et al.*, 1992. DW – dry weight

The concentrations of copper, lead and zinc in plants from the "Mina de Neves Corvo" site are in general higher in shoots than in roots, showing the present mining activity influence in the environment, probably also due to particles transportation by air.

In Brancanes site, the concentration in copper and lead in *Cistus ladanifer* was low and below the toxicity limit for plants. Once the soil available fraction for the same elements was lower than in "Mina de Neves Corvo", it seems that the soil-plant system already started the process toward a chemical equilibrium, after one century of abandon. In the other abandon sites of the Neves Corvo mining area, the natural attenuation is also running. However, data obtained by Batista *et al.* (2007) indicate that still exist acid generating materials in rocks and mine waste dumps in this abandoned area.

São Domingos Mine

São Domingos mining district is located in the Iberian Pyrite Belt, in southeast Portugal, some 60 km southeast of Beja (Fig. 1), about 5 km from the Spanish border. From the mining historical viewpoint, the São Domingos mine is one of the most emblematic and interesting abandoned mines in Portugal. The São Domingos deposit was a sub-vertical massive sulphide orebody located at the top of a Volcano-Sedimentary Complex sequence from Tournaisian age, represented by black shales, felsic, basic and intermediate volcanic rocks (Oliveira *et al.*, 2006; Matos *et al.*, 2006). The *gossan* and the supergene zone of the São Domingos orebody were mined since the Calcolithic, being intensively exploited for gold, copper and silver in Roman times. More recently, between 1857 and 1966, when the mine was closed due to the exhaustion of the reserves, mining activities were concentrated in the arsenic, copper, lead and zinc rich sulphide orebodies (Batista, 2000; Quental *et al.*, 2002). During the later period, and associated with the mining works several facilities were built, comprising a railway and the Pomarão river harbour (Guadiana river) for ore transportation, two pyrite burning factories (for copper concentration and sulphur extraction), the open pit (6.2 ha and 120 m deep), water reservoirs, cementation tanks, dams and network of channels for acid water evaporation, and the mining village (Mina de São Domingos). As a result of the intense mining activity a large negative environmental impact is still visible, mainly centred near the open pit, Moitinha (ore mills) and Achada do Gamo (pyrite burning factories) sectors, and along the São Domingos stream valley, where different type of materials, such as metallurgical slags, sub-grade ore, pyrite ash, *gossan* materials, and weathered host rock were deposited (Fig. 9). Part of the São Domingos village was constructed over *gossan* waste (around 14 Mm^3) (Quental *et al*., 2002; Matos *et al*., 2006; Álvarez-Valero *et al*., 2008). In the global area of the mine a total of 25 Mm^3 of mining wastes were estimated (Álvarez-Valero *et al*., 2008).

These mining residues were classified by Álvarez-Valero *et al*. (2008) in two main groups: industrial wastes derived from the ore processing, which includes Roman and modern slags, smelting ashes, pyrite-rich waste dumps, iron oxides, leaching tanks refuses, and industrial landfields; and mine wastes heaped as dumps, including *gossan* and sulphide disseminated host rocks. Recent mineralogical and chemical characterization of the São Domingos waste materials showed that most of them present potential for acid mine drainage (AMD) generation and consequently to the spread of hazardous chemical elements (antimony, arsenic, copper, iron, lead, tin, zinc). The typical mineral association in wastes is quartz, goethite, hematite, jarosite and mica, but depending on their origin, solid phases as feldspars, fayalite, glass, ore sulphides and secondary sulphate phases can be found (Rosado *et al*., 2008; Álvarez-Valero *et al*., 2008). The acid mine drainage and erosion processes of these materials resulted in soils, sediments and superficial waters contamination (Abreu *et al*., 2008; Batista *et al*., 2003; Quental *et al*., 2002; Quental *et al*., 2003).

Figure 9. São Domingos mine area — Achada do Gamo site with pyrite burning factories, slag heap and waste materials along the São Domingos stream valley.

Leachates from waste dump materials collected near the open pit and nearby Achada do Gamo presented very high concentrations of iron (median 3.4 g L^{-1}), sulphur (median 7 g L^{-1}) and aluminium (median 0.97 g L^{-1}), and relatively low concentrations of all other determined elements. Water leachates from gossanous materials showed high lead concentrations and from metallurgic slags showed high zinc and copper concentrations (Abreu *et al*., 2008). Seepage water flowing into the São Domingos stream, that drains the mine area, showed low pH (mean 2.6), and high values of Eh (mean 481 mV) and conductivity (mean 4337 µS cm^{-1}).

The extreme values of pH (1.7) and conductivity (14 800 mS cm^{-1}) were found in Achada do Gamo (Quental *et al.*, 2003). Groundwater showed high pH and redox potential, and low trace elements content, except for manganese, and in some locations also zinc, indicating that water contamination is confined to the main São Domingos surface waters (Martins *et al.*, 2007).

Table 17. Statistics of concentrations of chemical elements in soils (mg kg^{-1} DW) from São Domingos mine area

	As	Cr	Cu	Hg	Mn	Pb	Sb	Zn
Open pit site[(a)]								
Median	504	96	214.5	3.0	100	1597	145	118
Minimum	41.8	2.5	25.2	0.5	20	150	9.1	33.2
Maximum	11600	150	1275	11.0	1060	24930	2150	754
Achada do Gamo[(a)]								
Median	545	68	224	2	300	804	103	110
Minimum	25.9	29	56.6	0.5	300	95.7	6.0	28.0
Maximum	14200	195	6207	9300	2350	32170	5640	14850
Telheiro site[(a)]								
Median	277	75	50.3	0.5	430	156	68.9	88.7
Minimum	28.0	49	7.6	0.5	20	47.2	3.5	17.3
Maximum	15900	100	691	420	1140	7315	2400	495
UTPIA project[(b)]								
Median	22	65	27		548	42	2.8	62
Minimum	10	26	10	<1	24	18	1.2	31
Maximum	2570	93	1190	48	1930	25700	485	392
Abreu et al., 2008								
Minimum	175	–	25.2	<1	18.7	218	19.2	36.4
Maximum	11600	–	989	32	655	24930	2150	1369
Santos, 2007								
Minimum	1940	95	210	<1	48	5280	80.4	36
Maximum	3030	112	237	<1	62	9210	161	57
Freitas et al., 2004								
Median	353	8.3	444	–	–	2399	–	167
Minimum	37.2	5.1	87.3	–	–	234	–	104
Maximum	1291	84.6	1829	–	–	11218	–	714

[(a)]MINEO project (Quental *et al.*, 2002; Tavares, 2003; Tavares *et al.*, 2008); [(b)]UTPIA project (Martins *et al.*, 2008); DW – dry weight

A soil survey of the mine area was done within MINEO (Quental *et al.*, 2002; Tavares, 2003; Tavares *et al.*, 2008) and UTPIA (Martins *et al.*, 2008) projects, but other soil studies have also been fulfilled in some specific sites of the mine (Abreu *et al.*, 2008; Freitas *et al.*, 2004b; Santos, 2007). Soils were mainly developed on waste materials, weathered rocks mixed or not mixed with waste materials with different composition, and river bank sediments. As a consequence, soils presented a wide range of pH values (1.8 – 7.8) and, in general, low nutrient contents. Soils from the mine area are heterogeneous, due to different characteristics of original materials. They showed high total concentrations of trace elements mainly antimony, arsenic, copper, lead, zinc) (Table 17) that exceeded the normal values for a non-contaminated area of the region (Tavares *et al*., 2008). Some soils contain high mercury concentrations, especially those collected in Achada do Gamo subarea, where pyrite was burned, and also in Telheiro soils developed on riverbank sediments located downstream from Achada do Gamo.

Althought contaminated a great part of the São Domingos soils are relatively covered by vegetation. A sort of species colonizes, in general, soils developed on riverbank sediments, gossan materials, and mixtures of different waste materials and/or host rocks. However, slag piles and brittle pyrite are bare or contain very few plants. More than a hundred species were identified in the mine area (Veigas, 2005). Among them, there are some species that has been studied for elemental composition in order to evaluate their potential for soil remediation (Table 18) and have been recognized as tolerant to the mining environment where soils/wastes are contaminated and show low nutrient contents.

Plants from *Cistaceae* family (*Cistus ladanifer* L., *Cistus salviifolius* L. *Cistus crispus* L. and *Cistus monspeliensis* L.) are widespread in all the mine area growing on a diversity of substrata. C*istus ladanifer* and *C. salviifolius* (Fig. 10a) can be found even on fine slag materials, brittle pyrite and/or pyrite ashes with very high arsenic and lead concentrations (e.g. 7360 and 6000 mg kg^{-1}, respectively) and did not display visual symptoms of toxicity. *Cistus monspelienses* is frequently observed on soils developed on riverbank sediments. *Cistus ladanifer* plants can uptake and translocate to the aboveground part considerable quantities of lead (up to 279 mg kg^{-1}), whereas the other *Cistaceae* species attain the lowest lead concentrations (e.g. *C. salviifolius*: 14.3 mg Pb kg^{-1}). Nevertheless, these plants accumulate lead in root system beeing the concentration ratio of the element in aboveground part/root < 1. These plant species are also tolerant to arsenic, another major contaminant of the mine area, but the aereal part of the plants contains lower arsenic concentration than lead (Table 18).

a b

Figure 10. São Domingos mine area – waste materials colonized with: (a) *Cistus ladanifer*, *Cistus salviifolius*, *Erica australis*, etc.; (b) *Erica australis*, *Erica andevalensis* and *Quercus ilex*.

Two species of the genus *Erica* (*Ericacea* family) deserves special attention in São Domingos; *Erica australis* L. and *Erica andevalensis* Cabezudo & Rivera (Fig. 10b). The latter species was described for the first time in 1980 by Cabezudo & Rivera and grows on the banks of Tinto and Odiel rivers, as well as on mining tailings in the same zone being its distribution limited then to the mining region of Andévalo (Spain). Nowadays, the species can be found in almost all mine areas of the Spanish Iberian Pyrite Belt. *Erica andevalensis* was classified as an endangered species by the Andalusian (southern Spain) Regional Government, as its geographic distribution is limited to the pyrite mine environments (Aparício & García-Martin, 1996). In Portugal, this species was identified in São Domingos mine for the first time by Capelo *et al.* (1998), where it grows on soils developed on the sediments along the bank of the São Domingos river that carries acid water from the abandoned mine (Abreu *et al*., 2008) and, more recently on the slopes nearby. *Erica australis*, an endemic species in the Iberian Peninsula and NW Africa, is another spontaneous shrub very well established in São Domingos area, colonizing almost all kind of waste materials where it can attain up to 1–2 m high.

Table 18. Concentrations of chemical elements in the aboveground part of the plants (mg kg^{-1} DW) from São Domingos mine area

	As	Cu	Hg	Pb	Zn
Cistus crispus[(a)]	1.8	9.1	–	30	130
**Cistus ladanifer*[(a, b)] (L)	1.7–2.1	8.2–13.4	–	11.0–55.8	149–170
**Cistus ladanifer*[(c)] (A)	11.2–56.8	58–432	<1	20–279	659–1550
Cistus monspeliensis [(a)]	1.7	10.6	–	20.4	243
Cistus salviifolius[(a)]	1.5	14.9	–	14.3	178
**Erica australis*[(d)]	1.6–12.5	3.0–12.8	1.3–14.2	2.4–59.1	9.9–64.4
**Erica andevalensis*[(d)]	3.0–43	4.1–38.3	2.8–44.4	3.1–263	11.2–43.5
Genista hirsuta[(a)]	0.6	5.4	–	3.5	1329
Ulex eriocladus[(a)]	1.5	8.2	–	13.2	35.8
Genista polyanthos[(a)]	6.2	6.0	–	12.9	84
Lavandula stoechas[(a)]	0.9	7.0	–	15.7	139
**Lavandula luisieri*[(c)]	5–27.7	124–171	<1	17–153	533–1630
Thymus mastichina[(a)]	13.6	25.5	–	33.4	143
Helichrysum stoechas[(a)]	3.6	16.4	–	16.9	190
Agrostis castellana[(a)]	2.1	3.6	–	8.5	35.8
Rumex induratus[(a)]	1.4	21.1	–	7.8	25.9
Daphne gnidium[(a)]	1.2	10.7	–	9.5	202
Pistachia lentiscus[(a)]	0.9	8.5	–	7.2	30.7
Scirpus holoschoenus[(a)]	8.0	21.9	–	51.7	38.3
Juncus conglomeratus[(a)]	23.5	28.9	–	84.8	70.7
Juncus efesus[(a)]	8.5	18.0	–	22.4	96.1

*(minimum-maximum); [(a)]Freitas *et al*., 2004; [(b)] Santos, 2007; [(c)]UTPIA (Martins *et al*., 2008); [(d)]Abreu *et al*., 2008; (L) leaves; (A) aboveground part of the plant. DW – dry weight

Both species are well adaptade to the extreme mine environments with low pH (3.0–4.5) and high hazardous chemical elements contamination (Abreu *et al*., 2008): antimonium (19.2–2150 mg kg^{-1}), arsenic (175–11600 mg kg^{-1}), copper (25–989 mg kg^{-1}), lead (218–24930 mg kg^{-1}), zinc (36.4–1369 mg kg^{-1}), and mercury can reach 32 mg kg^{-1}.

Freitas *et al.* (2004) also reported other species, from the São Domingos mine area: *Quercus ilex* L. (arsenic: 1.2 mg kg^{-1}; lead: 7.2 mg kg^{-1}); *Eucalyptus camadulensis* Dehnh (arsenic: 0.6 mg kg^{-1}; lead: 3.0 mg kg^{-1}); *Eucalyptus globulus* Labill (arsenic: 0.4 mg kg^{-1}; lead: 4.5 mg kg^{-1}); *Pinus pinaster* Aiton (arsenic: 0.7 mg kg^{-1}; lead: 4.0 mg kg^{-1}); *Pinus pinea* L. (arsenic: 0.6 mg kg^{-1}; lead: 5.9 mg kg^{-1}).

Greenhouse pot experiments were conducted using São Domingos soil developed on a mixture of gossan materials and host rocks, and different levels of insoluble polyacrilate polymers, with the main goal of remediation (Guiwei *et al*., 2008). Soil presented high concentration of total lead (6.2 g kg^{-1}) and orchardgrass (*Dactylis glomerata* L. ev. Amba) grew poorly on the unamended soil. The polymers increased soil water holding capacity and the quality of the soil was improved, as evaluated by plant growth stimulation and soil organisms. The soil lead available fraction was also slightly reduced. The polyacrylate polymers could be a main advantage in mine areas from a semi arid region as is the case of the São Domingos mine; they can provide a medium for soil water retention, probably decreasing trace elements leachability, improving soil quality and consequently vegetation establishement.

In spite of the high concentrations of hazardous chemical elements in São Domingos soils/wastes none of the spontaneous plants growing in the mine area are arsenic or lead accumulators. The concentrations of arsenic, copper, lead, manganese and zinc in the aboveground part of the plants are below the range of domestic animal toxicity. Some *E. andevalensis* plants are an exception because the arsenic and lead concentrations were higher than 30 and 100 mg kg^{-1}, respectively. In addition, among the plants identified in the mine area some are autochthon and pioneer species; they can be the key for stabilization and environmental rehabilitation of these degraded and contaminated areas, because they can contribute for ecological succession evolution by increasing weathering conditions and pedogenesis.

CONCLUSION

The sustainability of phytostabilization programs in mine tailings should combine different processes and approaches (physical, chemical and biological) being able to ameliorate multiple constraints of this adverse media, such as toxicity due to a multiple hazardous chemical elements contamination, and water and nutrient deficiency. Effective phytostabilization requires a thorough understanding of the characteristics of soil/spoil, including the chemistry of soil contaminants, soil amendments, and tolerant plant species, the chemistry and microbiology of the rhizosphere and root exudates, in order to prevent further unintended effects that might increase contaminant solubility and leaching, as was observed for arsenic in the Jales mine. Successful plant establishment in mine tailings or other degraded areas by suitable amendment addition should also create an abundant and diverse heterotrophic microbial community. This synergistic effect might control the trace elements bioavailability in the rhizosphere contributing to reduce leaching, allowing plant growth and adding for ecological succession evolution. Moreover, it can also improve waste materials weathering and other biogeochemical processes leading to a faster soil formation.

An adequate choice of plants, focused mainly on native, pioneer, and tolerant species growing in the degraded areas with or without suitable amendments must be a remediation approach for mine tailings. In the Portuguese mines several plant species, well adapted to the extreme conditions found in those areas, were identified, and can be used for phytostabilization purposes. In the north of the river Tejo where the climatic conditions are moister than in the south, the most widespread plants are: *Arbutus unedo*, *Cistus inflatus*, *Cistus ladanifer*, *Cytisus multiflorus*, *Cytisus striatus*, *Erica arborea*, *Erica australis*, *Erica lusitanica*, *Ulex* spp., *Calluna vulgaris* as shrubs; *Quercus pirenaica*, *Quercus robur*, *Pinus* spp. as trees; and several grasses (*Poaceae* family). In the south of river Tejo, with semiarid conditions, dryer climate than in the north, the species that seems well adapted to the edaphoclimatic conditions are: *Erica andevalensis*, *Erica australis*, *Cistaceae* family plants (*Cistus ladanifer*, *Cistus salviifolius*, *Cistus crispus*, and *Cistus monspeliensis*), *Lavandula luisieri*, *Genista* spp. as shrubs; *Pinus* spp., *Quercus ilex* and *Quercus rotundifolia* as trees; and several grasses mainly of *Poaceae* family. In the wet areas, bording the water bodies or streams, *Juncos* spp., as well as other plants, like those from *Ericaceae* family (e.g. *E. andevalensis*) are species, well adapted to extreme pH and trace elements content of sediments/soils that could be used in the recovery of the mining areas. *Eucalyptus* and *Pinus* trees can also be used in both climatic areas as introduced species with economic profit together with endemic shrubs in phytostabilization programs.

The evaluation of how the phytostabilization process affects the long-term fate of amendments and metal contaminants in terms of mobility and speciation is yet one area not always well studied (Mendez & Maier, 2008a). A long-term monitoring plan for the evaluation of vegetation responses and basic tailings chemistry as affected by phytostabilization needs to be taken into account in the phytostabilization design.

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