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A biogeochemical approach for the environmental characterisation of mine lands

Ph. D. Thesis

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A Stefano e tutta la mia famiglia

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Abstract

Abstract

The determination of PTE environmental impacts at mine lands is a complex issues, since it regards different environmental matrix, as earth material (soils and waste-rocks), superficial and underground waters and also living beings. All of these can be investigated by biogeochemical tools, as they are very useful to understand how PTE move from waste-rocks to the surrounding ecosystems and how a careful mine land management can control their impacts.

This project was carried out in order to check and develop analytical methodologies for the evaluation of:

1. PTE contamination of earth materials (soil or waste rock), with a special care for arsenic, one of the most dangerous elements for human health;
2. AMD evaluation, by the application of different analytical methodologies (static and kinetic tests);
3. biogeochemical features of wild flora growing on mine sites, in order to collect useful information for mine lands remediation.

AMD evaluation was done by the applications of AMIRA procedure (IWRI & EGI, 2002), that allowed to identify the acid production or neutralising potential of earth materials. Moreover, an important tool for geochemical assessment of abandoned mine-waste dumps was applied, as it is a quick, cost-effective and qualitative leach procedure, designed by the Environmental Protection Agency (1994) to evaluate the impact of contaminated earth material on groundwaters. This kinetic test provides an insight into the behaviour of the waste-rocks during the interaction with meteoric water and gives useful indication of the potential chemical composition of the run-off from the weathered surface of mining areas.

Moreover, the relationship between earth materials and plants growing on mine areas were investigated and metal tolerance strategies were identify by the calculation of the appropriate biogeochemical parameters as Bioaccumulation Factor and Traslocation Factor.

These approaches have been developed on two ancient mine sites, with different geo-environmental setting: Rosia Montana mining area (Romania) and Gromo-Gandellino mining area (Valseriana, Northern Italy).

Rosia Montana mining area (Romania) is a hydrothermal gold deposit hosted in andesites and dacites of Neogene age, piercing the pre-volcanic sedimentary basement as breccia pipes, that host polymetallic sulphides and Au-Ag-Te mineralisations. Century of exploitation caused a significant environmental damage and the excavation and exploitation of tunnels and open pits has generated a large amount of waste-rocks dumps, some of them located close to villages. Private company provided remediation plans for the past mining activity and mitigation plans for reopening.

Gromo-Gandellino ancient mining area is a Ag – Fe ore deposit made up mainly by sulphide, sulphosalts and carbonate, intensely exploited in the medieval epoch and abandoned in the early decades of 20th century. The area is not exploited at the present time, but the numerous underground cavities and waste-rock dumps, some of them located very closed to villages, testify the historical activities linked to the exploitation of Fe, Zn, Pb, Ag and Cu mineralisations.

At Hop waste-rock dump (Rosia Montana mine site, Romania) the spatial heterogeneity is well represented. Earth material is composed by two different rock types: (1) the so-called WR1 samples, a source of acid drainage ; and (2) the WR2 samples, able to buffer the production of acidic water. On the whole, Hop waste rock dump is however a source of acid drainage, as showed both by static and kinetic tests. These last have confirmed to be an important tools for geochemical assessment of abandoned mine-waste dumps, as they are a quick, cost-effective and qualitative leach procedure to evaluate the impact of contaminated earth material on groundwater and to assess metal mobilisation from waste-rocks.

The tree species growing on Hop waste-rock dump, belonging to *Salix* spp., *B. pendula* and *P. tremula,* are able to tolerate limiting conditions (such as acid pH values and mean As content of 80 mg/kg), as known from the literature. They actively accumulate Cu and Zn in their tissues, specially in leaves, although they can not be considered as hyper-accumulators. On the other hand, the same species act as excluders for As, whose concentration in plant tissues are lower than in soils, exceeding however toxic values. *Salix* spp. represents the species more able to tolerate different environmental situations and to grow on strong acid substrates, acting as a pioneer species that could be used for revegetation of mine lands and stabilization of dump slopes, even on the area still not vegetated.

At Gromo-Gandellino mine site, the occurrence of waste-rock dumps represents an environmental hazard for the area: soil heavy metal concentrations is about one order of magnitude higher than in natural soils, specially at Coren del Cucì site, located in the vicinity of Gromo village.

The mining area is colonised by the metal tolerant species *C. vulgaris* and *D. filix-mas*. These plants behave as excluders and accumulation occurs only in roots, where internal metal detoxification mechanisms might exist in addition to exclusion strategies. So, they can be used surely as slope dump “stabilizators” and, in particular, *C. vulgaris* appears interesting for mine land restoration and soil stabilization of Cu, Zn, Pb, Ni, Cd and As.

The biogeochemical characterisation of these mine lands gave useful information to support their management, as it provided information for the choice of sites that need priority remediation activities, and identified, within these sites, the areas responsible for contamination. Moreover, the identification of metal tolerance species and their strategies provided useful information for project of rehabilitation, but also highlighted how PTE move through food webs.

Introduction

Abandoned mine lands are often perceived to have significant environmental impacts, particularly on superficial and ground waters, from water contaminated with acid and elevated metals flowing from leaching waste dumps and from underground mine workings. As a matter of facts, metals and metalloids, also called Potentially Toxic Elements (PTE), can affect organisms that move into contact with them, as plants, animals and living beings. Moreover, the development of Acid Mine Drainage (AMD) with consequent release of PTE, as a result of the oxidative weathering of sulphides, is one of the main environmental problem affecting the natural watercourses in mining areas. These conditions would require risk assessment and remediation in case of necessity.

Taking into account the particular features of these areas (characterised by natural high PTE concentrations) and environmental law problems (the inability of agencies to cite or allocate clear ownership for the problems at the sites), rises the need to improve their environmental characterisation, to supports their management and/or their remediation. In particular, biogeochemical tools can collect useful information for the development of phytoremediation methodology, an innovative technique based on the use of plant-base processes to diminish, remove, contain, inactivate or destroy PTE in soil *in situ*. Plant species used in phytoremediation projects are able to survive and reproduce themselves on contaminated substrates, by the developed of different metal tolerance strategies, based on accumulation or exclusion mechanisms.

The main problems related to mine lands comprise:
the identification and characterisation of mine dumps, the waste products of exploitation, composed mainly

- of rocks with PTE concentration too low to be economic but rather high to be a source of environmental pollution;
- the assessment of PTE concentrations and mobility;
- the assessment of Acid Mine Drainage production potential;
- the accumulation of PTE into living beings and their moving through food webs;
- the identification of species suitable for rehabilitation and remediation projects.

This project was carried out in order to check and develop analytical methodologies for the evaluation of:

1. PTE contamination of earth materials (soil or waste rock), with a special care for arsenic, one of the most dangerous elements for human health;
2. AMD evaluation, by the application of different analytical methodologies (static and kinetic tests);
3. biogeochemical features of wild flora growing on mine sites, in order to collect useful

4. information for mine lands remediation.

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Chapter 1

Mining activities and environment

1.1 Ore deposits and mining activities

A mineral deposit is an anomalous concentration of metal minerals (Guilbert & Park Jr., 1986). It becomes an “ore deposit” if (1) it contains elements or minerals that are useful and valuable; (2) occurring in a form, with a grade and tonnage that allow their exploitation, transport and processing; (3) could be exploited with the existing technologies (Guilberg & Park Jr., 1986; Evans, 1987; Craig et al., 1996; Robb, 2005).

The evaluation of an ore deposit depends on many geological, social, economic, technological and environmental factors (Evans, 1987). The working steps regarding its exploitation comprise: mining, mineral processing, metallurgical extraction and disposal of gangue materials, made by waste rocks and tailings.

1.1.1 Extraction

Mining is the first operation in the commercial exploitation of ore minerals. It is defined as the extraction of materials from the ground, in order to recover one or more component parts of the mined material. Mining techniques can be divided into two basic excavation types: 1) surface mining and 2) underground mining.

Surface mining generally involves open pit, developed as conical chasms with terraced benches that spiral downward to the bottom of the pit. These benches serve as a haulage roads and working platforms on the steep sloping sides of the pit. Extraction proceeds by drilling, blasting and loading material into trucks. This technique is an economically method of extraction involving large tonnages of ore and high rates of production. Surface mining is preferred to underground mining when the ore is at low depth because is less expensive and safer. However it often results in a greater environmental impact than underground mining

(Craig et al., 1996).

Underground mining, involving a system of subsurface workings, is used to extract ore minerals that cannot be found near the surface. Most mines consist of one or more means of access via vertical shaft, horizontal adits or inclined roadways. These provide transportation of men, machinery, materials, extracted ore and wastes. They also form part of the system of ventilation and the control of underground water that are essential to mining operation. Shafts, adits and roadways lead to the region where ore is extracted that is referred to as a stop. Usually there are intersecting horizontal tunnels (drifts and cross-cut) often on several levels joined by further vertical openings (raises or winzes). The greatest problems related to underground mining, in addition to air and water, are the increasing of the temperature with the depth and the potential rock-falls and cave-ins (Craig et al., 1996).

1.1.2 Mineral processing

Mineral processing aims to physically separate the ore minerals from gangue material and concentrate ore mineral for the following treatments. Dividing and concentrating processes are based on the physical properties of the minerals that occur into the ore and include magnetic separation, gravity separation and flotation.

Taking into account the researched mineral/element, the economic conditions and the available technologies the ore mineral could be divided in two portions: the first one with a grade of researched mineral over the cut-off value, called “concentrate”, and the second one with a grade of researched mineral under cut-off value, called “waste rocks”.

1.1.3 Metallurgical treatment

Metallurgical extraction aims to destroy the crystallographic bond of the ore minerals, in order to recover the sought after element or compound. Extractive metallurgy is largely based on hidrometallurgy (e.g. Au, U, Al, Cu, Zn, Ni, P) and pyrometallurgy (e.g. Cu, Zn, Ni, Pb, Sn, Fe), and to lesser degree on electrometallurgy (e.g. Al, Zn) (Ripley et al., 1996; Warhurst, 1999). The discard of any metallurgic treatment is termed “tailing”.

1.1.4 Disposal

Mine activities produce “mine waste”: solid, liquid or gaseous by-products of mining industry. Solid mine waste can be used for fill the opening created by the mining (backfilling), but their disposal usually involves dumping the waste at the surface next to mine workings. Only few time they could be used to fill lands, because they must not contain 1) acid-generating mineralogical phases (e.g. pyrite); 2) high concentration of metallic mineralogical phases and 3) chemical substances used for separation of different elements that could be hazardous for the environment.

1.1.5 Closure

Mining works could come to the end for different main reasons: the resource exhaustion or the change of another variable (social, economic, technological or environmental).

1.1.6 Rehabilitation and reclamation

After closure every mine lands should be submitted to rehabilitation or reclamation workings.

Land rehabilitation is the process of returning the land in a given area to some degree of its former state, after some process has resulted in its damage. While it is rarely possible to restore the land to its original condition, the rehabilitation process usually attempts to bring some degree of restoration.

Land reclamation is instead the process of creating useful landscapes that meet a variety of goals, typically creating productive ecosystems (or sometimes industrial or municipal land) from mined land.

1.2 Mine waste

1.2.1 Classification

Mine waste can be further classified as: solid mining, processing and metallurgical wastes and mine waters (Lottermoser, 2003).

Mining wastes

This type do not contain ore minerals or their concentration is sub-economic. Mining wastes include *overburden* and *waste rocks*, removed to access the mine ore from underground and surface operations (especially open pits). They are heterogeneous geological materials and may consist of sedimentary, metamorphic or igneous rocks, soils and loose sediments, with particle sizes range from clay to boulder fragments. Their physical and chemical characteristics vary, according to their mineralogy and geochemistry, type of mining equipment and particle size.

Processing wastes

They are defined as the portion of crushed, milled, ground, washed or treated resource deemed to poor to be treated further, including 1) tailing; 2) sludge; 3) waste waters. In particular, tailings are defined as the processing waste from a mill, washer or concentrator that removed the economic metals and minerals.

Metallurgical wastes

This waste type is the residues of the leached or smelted resource deemed to poor to be treated further. At many gold mines hydrometallurgical extraction is performed, and hydrometallurgical waste are accumulated on site.

Mine waters

Mine waters originates as ground or meteoric waters, which run off or flow to a portion of a mine site, undergoing compositional modifications due to mineral-water reactions. The term “mine water” is collective and includes any water at mine site, including surface water and subsurface ground water (Morin and Hutt, 1997). Mine water terminology is shown in Table 1.1.

Type of mine water (Lottermoser, 2003)	
Mine water	Any surface water or ground water present at mine site
Mining water	Water that had contact with any of the mine workings
Leachate	Mine water that has percolated through or out of solid mine wastes
Effluents	Mine water that is discharged into surface waters
Mine drainage water	Surface or ground water that actually or potentially flows from the mine site into surrounding areas
Acid mine drainage (AMD) water	Low pH surface or ground water that formed from the oxidation of sulphide minerals and that actually or potentially flows from the mine site into surrounding areas

Table 1.1. Mine water terminology

1.2.2 Production

The exploitation of minerals resources results in the production of large volumes of mine waste, which represents the greatest portion of waste produced by industrial activity. For example, the Canada copper mine (Sonota state) produced approximately 6.552 million metric tons of waste (1926 data), and current waste production from the Colorada mine is around 2,36 million per year (Carrillo Gonzales & Gonzales-Chávez, 2006 and references therein).The EPA Toxic Release Inventory (2002) reported that in 2000 the hard-rock mining industry was the largest producer of toxic waste that year, releasing 1.5 million metric tons, or 47% of the total waste released by the United State (US) industry. Worldwide, metal contamination from mine tailings in the same year ranged from 10,000 to 600,000 metric tons of various metals (As, Cd, Cu, Ni, Pb and Zn) (Warhust, 1999).

1.3 Acid Mine Drainage (AMD)

1.3.1 AMD processes

Acid Rock Drainage (ARD) is a natural set of processes, occurring when sulphide-bearing mine waste (principally pyrite [FeS_2]) are exposed to oxidising conditions. The oxidation of sulphide minerals generates acid waters containing high concentrations of sulphates and metals. Potential sulphide-bearing materials include waste rock from overburden, interburden and processed ore (tailings). In some situations, low-grade ore stockpiles, open pits and exposed rock in underground mines may generate acidic conditions (Gray, 1997).

In mining areas these processes are very intensive and they are called Acid Mine Drainage (AMD). Prior to mining, oxidation of sulphide minerals and the formation of sulphuric acid is a function of natural weathering processes. The oxidation of undisturbed ore deposits, followed by the release of acid and mobilization of metals is slow. Natural discharge from such deposits poses little threat to receiving aquatic ecosystems, except in rare instances. Mining and mineral processing operations greatly increase the rate of these same chemical reactions by removing large volumes of sulphide rock material and exposing increased surface area to air and water.

1.3.2 Reactions

According to the reviews in AMD given by Nordstrom & Alpers (1999) and Blowes et al. (2003), pyrite oxidation must be considered the main cause of ARD or AMD processes. Even if pyrite is not the most reactive mineralogical phase (Jambor & Blowes, 1994), it is however the most common sulphide phase in ore deposits.

Pyrite oxidation is a complex process that can involve chemical, biological and electrochemical reactions. The simple pyrite oxidation by atmospheric oxygen and water is:

$$2\ FeS_{2\ (s)} + 7\ O_{2\ (g)} + 2\ H_2O_{\ (l)} \rightarrow 2\ Fe^{2+}_{\ (aq)} + 4\ SO_4^{2-}{}_{(aq)} + 4\ H^+_{\ (aq)} \qquad (1)$$

The Fe^{2+} thus released may be oxidised to Fe^{3+}:

$$4\ Fe^{2+}_{\ (aq)} + O_{2\ (g)} + 4\ H^+_{\ (aq)} \rightarrow 4\ Fe^{3+}_{\ (aq)} + 2\ H_2O_{\ (l)} \qquad (2)$$

Fe^{3+} oxy-hydroxides may precipitate:

$$Fe^{3+}_{\ (aq)} + 3\ H_2O_{\ (l)} \rightarrow Fe(OH)_3 + 3H^+ \qquad (3)$$

Adding equations 1-3 yields the overall reactions:

$$4\ FeS_{2\ (s)} + 15\ O_{2\ (g)} + 14\ H_2O_{\ (l)} \rightarrow 8\ SO_4^{2-}{}_{(aq)} + 4\ Fe(OH)_3 + 16H^+ \qquad (4)$$

From these reactions it is clear that pyrite can remain in its reduced state in undisturbed earth materials, so long as they are in an anaerobic environment.

1.3.3 Factors

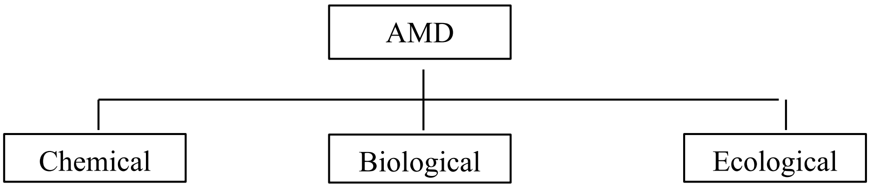
However, the factors that affect ARD or AMD processes are numerous and concern site features (location, climate, geology), physical features of reactive material (porosity, permeability, grain size) and chemical features of reactive material (mineralogy, weathering).

1.4 Environmental impact

1.4.1 Impact on soil, vegetation and animals

Mining activities affect relatively small area, but can have a large local impact on the environment. Release of Potentially Toxic Elements (PTE), as metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) and metalloids (As, Sb, Se, Te), occurs primary through: 1) AMD and 2) erosion of solid wastes (Salomons, 1995; Ripley et al., 1996).

Waste dumps and tailing deposits are subject to wind and water erosion, as well as to chemical reactions from exposure to air and water, with consequent generation of soluble acid or alkalis and soluble metal salts. The production of these reactions may be spread far from source location, with the potential to affects both the atmosphere, the hydrosphere (fresh or groundwater) and the lithospere, including soils and crop fields. Environmental effects of AMD are complex, but can be categorized as: 1) chemical, 2) biological and 3) ecological (Gray, 1997). Depending on the nature of waste rocks and tailing deposits, AMD can contain elevate levels of metal and metalloids: alteration of biogeochemical cycling is perhaps the most obvious environmental effects of mining, since an elements or compound is extracted from the ground and moved elsewhere (see figure 1.1).



Chemical	Biological	Ecological
Increased acidity Reduction of pH Destruction of bicarbonate buffering system Increase of soluble metal concentrations	Acute and chronic toxicity Death of senstivite species Acid-base balance failure in organisms	Habitat modifications Bioaccumulation within food chain Loss of food source or prey Elimination of sensitive species Reduction in primary productivity Food chain modification

Figure 1.1 : the major effects of AMD on ecosystems.

PTE in soils and sediments affect organisms on which they grown or move into contact with them, as shown in Figure 1.1. Plants are affected mainly by hydrospheric transfer from the lithospere to their roots, or atmospheric transfer to their leaves (Kabata-Pendias, 2011; Carrillo Gonzales & Gonzales-Chávez, 2006; Navarro et al., 2008). More over, some animals may absorb some substances directly through their skins or their digestive or respiratory systems, while feeding in an affected area (Kim et al., 2005; Kozlov et al., 2000; Pugh et al., 2002).

However, it is important to understand that the release of metals and metalloids from mine waste does not necessarily result in damage to the environment (Lottermoser, 2003). Many metals are essential for cellular function and are required by organisms at low concentration (Kabata-Pendias, 2011). It is only when the bioavailable content is excessively high that they have a negative impact on the health of organism and a toxic state might be reached. Processes that cause toxicity, disrupting ecological courses or posing a hazard to human health are referred to as “pollution”. On the other hand, “contamination” referes to processes which do not cause harmful effects (Thornton et al., 1995).

The extend and degree of PTE contamination around mine site vary depending upon geochemical characteristics and degree of mineralization of waste rocks and tailings (Johnson et al., 2000). Even the distance from a source at which metals affect plants can differ: near Flin Flon, Manitoba, for example, Mn was detectable about 250 km far from a smelter and Cu not more than 60 km away (Franzin et al., 1979).

1.4.2 Impact on human health

Mining affects human populations through: 1) fallout of gases and solid and 2) contamination of drinking water and crops, farm animals or food obtained in wild areas (Ripley et al., 1996; Jack et al., 2003 and references therein; Lee et al., 2005; Kien et al., 2009). PTE generally have several possible pathways, including inhalation, ingestion and absorption through skin.

Exposure to heavy metals is potentially harmful especially for those metal-compounds which do not have any physiological role in the metabolism of cells (e.g. As). The ingestion of metals via food or water could modify the metabolism of other essential elements such as Zn, Cu, Fe and Se. Furthermore, most metals are capable of forming covalent bonds with carbon, resulting in metal-organic compounds. Such a transformation influences their mobility, accumulation as well as their toxicity. Prolonged exposure to metals and metal compounds could result in disregulation of cellular pathways causing subsequent toxicity, regarding the functions of the central nervous system, the haematopoietic system, liver and kidneys (Florea & Büsselberg, 2006). Recently, more attention is given to metal compounds that have toxic effects at low levels of exposure (Kalia & Flora, 2005). In general, the toxic properties of metal-organic compounds differ from those of the inorganic forms. Due to their ability to reabsorb and accumulate metals, kidneys are one of the first target organs of metal toxicity, Furthermore, numerous authors described induction of genotoxicity and cytotoxicity by metallic species (Florea & Büsselberg, 2006 and references therein). Table 1.2 shows potential toxic effects of As, Pb and Cd which are environmental relevant elements to which humans could get exposed in mine lands.

Because of its toxicity, the potential As contamination of waster, air and soil from geological and anthropogenic sources is a significant environmental health concern. As contamination of groundwater, the a major source of drinking water in many parts of the world, has been reported in many cases, especially in the South East Asia Region Countries (SEAR). Contamination in SEAR countries occurred in Bangladesh, India (Ahmad, 2001; Garnier et al., 2011), Vietnam (Berg et al., 2001), Nepal (Tandurak & Neku, 2002), Taiwan (Chen et al., 1999) and PR China (Guo et al., 2001; Lin et al., 2002), where As is from natural sources.

PTE	*Potential toxic effects*	*References*
Arsenic (As)	• chronic poisoning (called arsenicosis) • skin lesions • damage to internal organs (respiratory, digestive, circulatory, neural and renal system) • skin, lung and bladder cancer	IPCS (2001) Jack et al. (2003) Florea & Büsselberg (2006)
Lead (Pb)	• damage to neurologic, hematologic and renal systems	CDC (2005) Florea & Büsselberg (2006)
Cadmium (Cd)	• heart and artery disease • high blood pressure • bone embrittlement • kidney disease • possibly cancer	Ripley et al. (1996) and reference therein

Table 1.2. Some effects of selected metals species and Arsenic on human health.

1.5 Environmental legislation

1.5.1 European legislation

Nowadays only few nations have a specific legislation, policy and guidance about risks related to mine lands. At the present, in the European Union a specific legislation for the management of waste from extractive industries has been published in 2006 (Directive 2006/21/EC).

The Directive 2006/21/EC provides for measures, procedures and guidance to prevent or reduce, as far as possible, any adverse effects on the environment (water, air, soil, fauna, flora and landscape) and any resultant risks to human health. Member State shall take the necessary measures to ensure that extractive waste is managed without risks for the environment and human health and prohibit abandonment, dumping or uncontrolled depositing of extractive waste. Each operator shall, before the start of the operations, draw up a waste management plan for the minimization, treatment, recovery and disposal of extractive waste, based on the best available techniques, taking into account the technical characteristics of waste facility, its geographical location and the local environmental conditions. The public shall be informed, by public notices or other appropriate means, of the decision concerning the management plan and its application.

1.5.2 Italian legislation

In Italy, before that article n.17 of D. Lgs. 22/97 took effect and became operative with D. M. 471/99, the environmental legislation faced the question of the potential contaminated sites in a fragmentary way, examining each case one at a time. D. Lgs. 22/97 and D. M. 471/99 established a standard procedure for the identification and characterisation of contaminated sites, the identification of toxic substances and the threshold concentration for contamination. Following the procedure proposed by these laws, the owner of a location that shows clues of a probable contamination must communicate it to the organisations (Province, Region, Environmental Agency). According to the organisation, the owner must execute the characterisation of the site, the sampling and the analyses of the environmental matrices (waters, soils and air). The site is defined as "contaminated" even if only one of concentration values of pollutant substances is higher than threshold concentration, established by D. M. 471/99. Taking into account that these threshold concentrations for contamination (CSC) were calculated supposing that in the site occur the worst conditions, sometimes must be started useless remediation procedures throwing away money (owner) and time (organisations).

With D. Lgs. 152/06 risk assessment is introduced to calculate threshold concentrations of contamination for each site (CSR). The first step is to identify the waste components at the source, including their concentrations and physical properties. After the source has been characterised, the pathways of the hazardous chemicals are analysed by quantifying the rates at which the waste compounds volatilise, degrade and migrate from the source. Finally, if the pathway analysis shows that the contaminant will come into contact with receptors; the hazard must be assessed with the aid of toxicological data (US EPA, 1989; Watts, 1998). If only one of concentration values of pollutant substances is higher than threshold concentration calculated after the risk assessment procedure, a remediation project must be edited.

However there is no specific legislation about the management of "abandoned mining sites" but only general legislation about "contaminated site remediation" or "waste disposal". There are several problems related to the management of mine lands. The first problem, in the case of an abandoned mine land, is related to the identification of the person or the company who is liable to pollution. This subject must pay for remediation. For legislation in force the liable of pollution is "who caused the exceeding of threshold concentration". But now, after thirty years or more since closure of mining districts, it is very difficult to find who is liable to pollution. The second problem is related to the concentration of heavy metals into all the environmental matrices since a mining site is a natural geochemical anomaly, so it is a mistake to classify an mine land as a potentially contaminated sites or as a contaminated sites taking into account only metal and metalloid concentrations into environmental matrices. Moreover, it is very difficult to calculate metal and metalloid background concentration values (EPA, 2000; Provincia di Milano & UNIMI, 2003; APAT & ISS 2006). The last problem is related to the cultural and historical heritage of mine areas. The remediation methodologies should be chosen not only for their efficiency, but also for their impact on morphology and structures of the AML that are considered cultural and historical heritage (D. Lgs. 42/04).

1.6 Conventional remediation methodologies and technologies

The main technologies for mitigation of AMD processes has been described by many authors (Johnson & Halberg, 2005; Li et al., 1997; Munro et al., 2004; Naftz et al., 2002; Swanson et al.; 1997 Von der Heyden, 2005).

1.6.1 Water treatment

The objective is to restore the water quality after it has been polluted.

Wetlands

Wetlands are areas that are inundated or saturated by surface or ground water, at a frequency and duration sufficient to support bacterial life to inhibit AMD reactions. Wetlands have the ability to remove metals from mine drainage and to neutralize AMD. Since wetlands are self-sustaining ecosystems, they may be able to remediate contaminated mine drainage as long as it is generated. Thus, they may represent a long-term solution to AMD, and to contaminated mine drainage in general. There are also numerous examples of failed designs of wetland treatment systems. There is not a clear evidence which demonstrates that wetlands uniformly ameliorate degraded mine drainage but, on the other way, there are small examples from many sources generally supporting this idea (Von der Heyden, 2005).

Permeable Reactive Barrier

In recent years, the difficulties of treating AMD (and other) contaminated groundwater has led to greater focus on the development of permeable reactive barriers (PRB). These passive treatment systems reduce or (potentially) eliminate on-going treatment costs and are designed to act as conduits for contaminated groundwater flow (US EPA, 1998). Contaminants can be contained (immobilized) and/or transformed (into non-toxic forms) within a PRB by adsorption, absorption, precipitation, redox, or biological processes (Puls, 1998) and represent a novel progression from inefficient groundwater pump and treat systems (NAS, 1994). Remediation of AMD with PRB generally relies on raising pH, and/or chemically- or biologically-induced sulphide precipitation (Naftz et al., 2002). Relying on a single process limits the suite of metals that can be effectively removed, so multi-stage PRB are commonly employed for AMD remediation (Munro et al., 2004 and references therein).

1.6.2 Water drainage control

The objective is to prevent contact between the reactive minerals and the water.

Dry cover – Soil cover systems

This technology consists in creating a “sealing layer” that covers the spoil that is usually constructed from clay. Dry covers used for surface storage of reactive mineral spoils may also incorporate an organic layer (MEND, 2000; Swanson et al., 1997).

Water cover system

Underwater storage has been used for disposing and storing mine tailings that are potentially acid-producing (Li et al., 1997). Again, the objective is to prevent contact between the minerals and dissolved oxygen. Shallow water covers may be used, and their effectiveness may be improved by covering the tailings with a layer of sediment or organic material, which has the dual benefit of limiting oxygen ingress and affording some protection against re-suspension of the tailings due to the actions of wind and waves (MEND, 2000).

Groundwater depression

This methodology consists in placement of sumps and pumping systems that allow the droop of water table under sulphide material.

1.6.3 Sulphide oxidation control

The objective is to prevent the acidifying reaction due to the contact between sulphide and oxidising waters.

Flooding

As much as both oxygen and water are required to perpetuate the formation of AMD, it follows that by excluding either (or both) of these, it should be possible to prevent or minimise AMD production. A way in which this may be achieved is by flooding and sealing abandoned deep mines. The dissolved oxygen present in the flooding waters (about 8–9 mg/l) will be consumed by mineral-oxidising (and other) micro-organisms present, and its replenishment by mass transfer and diffusion will be impeded by sealing of the mine. However, this is only effective where the location of all shafts and adits is known and where influx of oxygen-containing water does not occur.

Neutralisation

Another suggested approach for minimising AMD production is to blend acid-generating and acid-consuming materials, producing environmentally benign composites (MEND, 2000).

Coating

A variant on this theme is to add solid-phase phosphates (such as apatite) to pyritic mine waste in order to precipitate iron (III) as ferric phosphate, thereby reducing its potential to act as an oxidant of sulphide minerals. However, inhibition of pyrite oxidation using this approach may only be temporary, due to the process of “armouring” of the added phosphate minerals (Evangelou, 1998). Application of soluble phosphate (together with hydrogen peroxide) is one of the “coating technologies”: the peroxide oxidises pyrite, producing ferric iron, which reacts with the phosphate to produce a surface protective coating of ferric phosphate. An alternative technique involving the formation of an iron oxide/silica coating on pyrite surfaces has also been experienced.

Chapter 2

Biogeochemical features of mine lands

2.1 Geochemical behaviour of PTE in soils and aqueous solutions

2.1.1 Weathering processes

Soil is a very specific component of the environment, because it is not only a geochemical sink for PTE, but also acts as a natural buffer, controlling the transport of chemical elements to the atmosphere, hydrosphere and biota.

Weathering processes are the basic processes, responsible for the formation of soil from parent rocks and also for the alteration of waste rocks, resulting in increased mobility of metals and metalloids. Weathering has been extensively studied and reviewed as the complex interactions of the lithosphere, the atmosphere and the hydrosphere, that occur in the biosphere powered by solar energy (Kabata-Pendias, 2011 and references therein). The basic weathering processes reactions, such as dissolution, sorption, complexation, migration, precipitation, occlusion, diffusion (into minerals), binding by organic substances, absorption - sorption by microbiota and volatilization, are controlled by chemical equilibrium of the particular earth surface environment. The stability of such a system is mainly controlled by redox state (Eh) and buffer capacity (pH).

Moreover, micro-organisms (bacteria and fungi) and plants play a very important role in solubilising minerals, and thus, in the input of chemical elements to the soil solutions. These processes are known as “biological weathering” and two types of compounds released by organic matter or organisms are believed to be particularly involved in weathering processes: carbon acid, formed from CO_2 released during decay of organic matter, and organic chelates.

The second stage of soil formation processes (pedogenesis) results in the formation of a soil profile from the weathered rock material, leading to the development of a mature zonal soil.

Weathering and pedogenetic processes cannot be easily distinguished and separated, because they may take place simultaneously at the same sites and most commonly they are closely interrelated. However, the formation of soil from waste rock is a slow process and waste dumps are often characterized by low organic matter and the absence of soil profile.

2.1.2 Geochemical mobility and bioavailabilty

From an ecological and toxicological point of view, the most interesting fraction of trace metals is the "mobile fraction", as it is soluble and, through the aqueous solutions that circulate in the ground, could reaches living beings. For this reason, this fraction is also called "bioavailable" and its content is controlled mainly by: (1) the dynamic equilibrium between solid and liquid phases of the soil environment; and (2) the element chemical speciation (Schwitzguébel et al., 2002; Kabata-Pendias, 2011).

The dynamic equilibrium between solid and liquid phases of the soil environment are governed by several soil properties, of which soil pH and redox potential are known to be the most important parameters (Patrick et al., 1991; Bech et al., 1997). Thus, the solubility of trace metals is often shown as a function of pH, affected by the amount and kind of organic matter (van Herwijnen, 2007). More over, other soil factors such as cation exchangeable capacity (CEC), carbonates, Fe and Mn hydrous oxides, clay minerals, fine fractions and particle-size, are known to play significant roles in the behaviour of trace elements (Guo et al., 2010; Moreno-Jiménez et al., 2010; Garnier et al., 2011; Kim et al., 2011). The behaviour of trace elements in various weathering environments is shown in Table 2.1.

On the other hand, the definition of "speciation", in the context of soils and sediments, refers to the processes of identification and quantification of the different defined chemical species, forms and phases in which an element occurs in investigated materials (Ebdon et al., 2001). However, most often "speciation" also means the description of the amounts and kinds of existing forms of trace elements. Whichever approach is taken, the species, forms or phases are defined: (1) functionally; (2) operationally; and/or (3) as specific chemical compounds or oxidation states.

In order to assess the speciation of trace metals in solid materials, different analytical procedures have been developed (Tessier et al., 1979; Rauret, 1998; Rauret et al., 1999) and, despite all the limitations of these methods, some of them have been broadly used (Dold, 2003; Tarvainen & Kallio, 2002; Schultz et al., 2004; Menzies et al., 2007; Conesa et al., 2008 Rao et al., 2008; Guo et al., 2010). All procedures are based on the assumption that the following species of metals exist in soils as:

- water soluble (e.g., in soil solution);
- exchangeable;

- organically bound;
- occluded in Fe and Mn oxides;
- definite compounds (e.g., metal carbonates, phosphates, sulphides);
- structurally bound in silicates and/or other primary minerals (residual fraction).

The soluble exchangeable fraction characterizes the mobile species of metals in soils, while the other fractions are more or less immobile. The mobilization of metals from these fractions, or transformation of mobile to immobile metal species, is often a slow process, even if a relatively rapid transformation of metal oxide forms to more mobile carbonate species was also observed (Kabata & Kabata-Pendias, 1999). However, trace elements in soils and sediments are generally immobile and they can only affect organisms on which they are deposited or which move into contact with them.

Behaviour of PTE in various weathering environment		
Degree of mobility	**Environmental conditions**	**PTE**
High	Neutral or alkaline	Zn
Medium	Oxidizing and acid	Se, Cd, Hg, Cu, Ag and Zn
	Mainly acid	Ag, Au, Cd, Co, Hg and Ni
	Reducing	As, Cd, Co, Cr, Fe, Li, Mn and Sb
Low	Oxidizing and acid	Fe and Li
	Neutral or alkaline	Co, Cu, Mn, Ni and Pb
Very low	Oxidizing and acid	Al, Au, Cr and Fe
	Neutral or alkaline	Ag, Al, Au, Cu, Co, Fe and Ni
	Reducing	Ag, As, Au, Cd, Co, Cu, Hg, Ni, Pb, Se and Zn

Table 2.1: Behaviour of PTE in various weathering environment (from Kabata-Pendias, 2011 and references therein).

2.1.3 Dispersion processes

The transport of dissolved trace elements may take place through the soil solution, by diffusion, mass flow and leaching processes. Generally, in soils formed under a cool and humid climate, the leaching of trace elements downward through the profiles is greater than their accumulation, unless there is a high input of these elements into the soils. On the other hand, in warm and dry climates, and also to some extent in humid hot climates, upward dislocation of trace elements in the soil profiles is the most common movement. The rates of trace element downward migration are affected by chemical, physical, and biological soil properties (Navas & Machín, 2002), of which the most important are Eh–pH system, CEC and salt content, the amount and quality of organic matter, water and temperature and biological activities.

Impoverishment of soils in trace elements is mainly due to their mobility downward with percolating waters through the profiles and also due to trace element uptake by plants. In acid soils (e.g. with pH below 6.5), several elements such as Zn, Mn, Cu, Fe and Co are easily leached. These elements, however, form quite stable compounds if the pH of the soil rises above 7. Other elements, such as Mo, Se and As, are mobilized in alkaline soils, while in acid soils they become almost insoluble.

At mine lands, AMD processes can cause an increase in acidity of soil solutions, with a consequent increase in the mobility and dispersion of PTE and alteration of biogeochemical cycling (Salomons, 1995; Gray, 1997). As a matter of facts, plants can be affected by these alterations , as they have a remarkable skill to absorb and accumulate inorganic compounds from the substrate on which they grown.

2.2 Mine land vegetation

Ecological studies revealed that metalliferous mine wastes can be colonized by plants, starting with seeds or vegetative propagules, that comes from the surrounding vegetation or after long-distance transport by wind and water (Marrs & Bradshaw, 1993; Bradshaw, 1997). The ecological succession on waste dumps and tailings is very slow, due to their slope, the lack of organic matter and high PTE concentration. However, this type of substrate can select a specific assemblage of plant species, which show adaptation to environmental stress, especially to metal toxicity.

2.2.1 Metal toxicity

As a matter of facts, some trace elements, such as Cu, Ni and Zn, are essential nutrients for plants, but they become environmental pollutants and phytotoxic when they reach threshold concentrations in the soil. On the other hand, metals and metalloids such as As, Cd, Co and Pb are toxic even at very low concentrations. Many observations have been published on the harmful effects of trace element excesses and their basic reactions

(Kabata-Pendias, 2011 and references therein). Visible symptoms of toxicity vary for each species and even for individual plants, but most common and significant effects of the excess of trace metals are: (1) damage to photosynthesis apparatus involved in several metabolic alterations; (2) damage to root system; (3) inhibition of seed germinations; and (4) reduce of growth. The most toxic metals for both higher plants and micro-organisms could bring to their death and they are Hg, Ni, Pb, Co, Cd, Ag (Kabata Pendias, 2011) and As (Meharg & Hartley-Whitaker, 2002).

2.2.2 Metal tolerance

Some species and ecotypes are able to grow and reproduce themselves on substrates characterized by high metal concentrations, such as waste dumps and tailings, despite their high PTE contents. These species are called “metallophyte” and grow on mineralized, heavy-metal-polluted, mine and smelter areas, developing mechanisms that allow them to tolerate high metal concentrations, which are toxic for many plants (Baker &Brooks, 1989; Brooks, 1998). This skill is called “metal tolerance” and it has been reviewed in detail by Baker (1987) and applied by many other authors (Antosiewicz et al, 2000; Del Rio et al., 2002; Carrillo Gonzales & Gonzales-Chávez, 2006; Cornara et al., 2007; Brunetti et al., 2009; Moreno-Jimenéz et al., 2010).

Resistance to PTE implied the development of a specific genetic basis (Baker, 1987), that regardless evolved in different taxa (Ernst et al., 1992) and is based on accumulation or exclusion mechanisms.

Accumulation

Accumulator species are able to concentrate and detoxify very high contents of metals and metalloids in their aerial tissues, by the possession of specific physiological mechanisms which ensure the correct functioning of vital activities despite high PTE concentrations. These species are characterized by a slow growth rate and a low biomass production, as the result of the expenditure of energy necessary to the operation of the mechanisms of tolerance involved.

Some species, called “hyper-accumulator”, are able accumulate very high concentration of metals and metalloids in their aerial tissues, that far exceed the physiological levels found in many species (Kabata-Pendias, 2011). Trace element concentrations in in their tissues are higher than 100 mg kg^{-1} for As and Cd, higher than 1,000 mg kg^{-1} for Co, Cu, Ni and Pb, higher than 10,000 mg kg^{-1} for Zn (Brooks, 1998; McGrath & Zao, 2003). Hyper accumulators also show BF values >> 1. Metal concentration in shoots normally exceed those in roots, and it has been suggested that metal hyper-accumulation has the ecological role of providing protection against fungal and insect attacks (Chaney et al., 1997).

More than 400 hyper-accumulator species has been identified (Brooks, 1998) and the list is still growing. Examples include species of *Thlaspi* (Brassicaceae), which can accumulate more than 3% Zn, 0.5% Pb and 0.1%Cd in their shoots (Baker et al., 1991; Brown et al., 1994) and *Alyssum* (Brassicaceae), some species of which have been shown to accumulate over 1% Ni (Brooks et al., 1979).

Exclusion

The *excluders* are able to restrict the metal uptake and their transport from roots to leaves, maintaining a low shoot levels over a wide range of soil concentrations. These species are able to reduce the mobility and bioavailability of PTE, either by immobilization in the rhizosphere or by prevention of migration. This strategy is often applied with the contribution of biotic interactions between plants, bacteria and mychorrizal fungi, which play a key role to decrease the phyto-toxic of PTE.

For instance, species of Ericacea family (Abreu et al., 2008) are characterized by a constitutive metal tolerance based on exclusion mechanisms. In particular, the species *Calluna vulgaris* was observed to be very tolerant to heavy metals occurring on different substrates, as serpentine and polluted soils (Monni et al., 2000). More over, it uses to form an ericoid mychorrizal association (ERM) with the fungal *Hymenoscyphus ericae* that plays an important role in metal tolerance, by preventing metal translocation to the growing parts of the plant, allowing the accumulation of high concentrations of Cu (Bradley et al., 1982; Pratas et al., 2005).

2.2.3 Phytoremediation

Phytoremediation is an innovative methodology, based on the use of plant-base processes to diminish, remove, contain, inactivate or destroy PTE in soil *in situ* (Schwitzguébel et al., 2002). It may be employed by using two different approaches: phytoextraction and phytostabilization. Wild flora should be used in both cases, because is adapted to soil and climatic conditions and improves local biodiversity (Kucharski et al., 2005; Abreu et al., 2008).

Phytoextraction

Phytoextraction is a technology that use plants and their associated rhizosphere organisms to remove contaminants from soils. This is done with accumulation or hyper-accumulation of PTE in the aboveground plant biomass (Cummingham et al., 1995). Plants are then harvested and disposed as hazardous waste or incinerated for metal recovery. An ideal plant species for phytoextraction should possess the following features:

1. tolerance to the metal concentrations accumulated;
2. fast growth and highly effective metal accumulating biomass (however, hyperaccumulator species are often characterized by a slow growth and a poor biomass production);
3. accumulation of metal in the above ground parts;
4. easy harvest.

Phytostabilization

Phytostabilization is a technology that use plants, their associated rhizosphere organisms and soil amendments to reduce metal bioavailability and the related hazard (Schwitzguébel et al., 2002). Processes like root-adsorption and plant-induced chemical changes in the rhizosphere decrease metal mobility, also reducing the likelihood of toxic elements entering into the food chains and the risk to human health (Cunningham et al., 1995). Plant species suitable for phytostabilization are characterized by a remarkable roots development and do not concentrate elements in leaves, seeds or other parts that could be eaten by humans or animals. Moreover, phytostabilization has the advantage, compared to other phytoremediation techniques, to eliminate the need of treating harvested shoot residues as hazardous waste.

Advantages

One of the advantages of phytoremediation is the low cost of its implementation, as compared to traditional engineering practices that rely on intensive soil manipulation. While traditional remediation technologies are expensive and affect only the upper layers of soil, phytoremediation could be an effective, long-term and relatively low-cost management strategy (Bradshaw, 1993).

Another advantage is the environmental benefits, because phytoremediation is considered a low impact technology, that promotes biodiversity conservation (Whiting et al., 2004) and brings to a visual landscape improvement. At mine lands, the restoration of a vegetative cover can reach also the objectives of stabilization of waste dump slopes and reduction of PTE dispersion, water-leaching and wind erosion.

Obstacles

Large scale application of phytoremediation involves some significant obstacles, such as the long time required for remediation and the levels of PTE tolerated by the plants employed. For instance, *Thlaspi caerulescens* is a known Zn hyper-accumulator, but its use in the field is limited because individual plants are very small and slow growing (Ebbs & Kochian, 1997).

Furthermore, soil treatments are often limited to the bioavailable fraction of the trace elements, that could be increased by artificial surfacactants, biosurfactants or soluble organic matter produced by microbes and plants. In contrast to synthetic additives, substances excreted by bacteria and plants are continuously produced *in situ* and are often non-toxic (Schwitzguébel et al., 2002). However, an increased bioavailability may be dangerous, since it can result in a progressive leaching of PTE, and surrounding soil or groundwater might become contaminated. Therefore, a risk assessment should be included before using surfactants or other mobilizing agents on a large scale.

Application to mine lands

Phytoremediation methodologies have been applied to mine lands, as reviewed by Mendez & Mainer (2008). These studies suggest that phytoextraction should be limited to sites that have high land values and for which metal removal is required, due to its high implementation costs and long time frames. On the other hand, phytostabilization is characterized by lower cost and easier implementation and could be a more commonly used approach. However, complete restoration of mining sites is an unlikely outcomes for either approach.

Chapter 3

Biogeochemical characterisation of mine lands

3.1 Objectives and methodologies

The biogeochemical characterization of sulphide mining areas is an essential tool, that allows to assess the associated geochemical risk and provides useful information for their proper management and rehabilitation.

Dynamic and complex interactions between waste-rocks and water circulating underground deserve special attention, as they are responsible for the dispersion of PTE in the environment and the formation of acid waters and AMD processes.

The relationship between earth materials (waste-rocks or soils) and plants growing on mine areas are very important too, because plants uptake eco-toxic elements from substrates and transfer them to animals and humans, through the food webs. On the other hand, metal tolerant native species could be suitable for mine land remediation and rehabilitation.

This project was carried out in order to check and develop analytical methodologies for the evaluation of:

1. PTE contamination of earth materials, with a special care for arsenic, one of the most dangerous elements for human health;
2. AMD evaluation by the application of different analytical methodologies.
3. biogeochemical features of wild flora growing on mine sites, in order to collect useful information for mine lands remediation.

To characterise the main biogeochemical features of mine lands the following steps were performed by an integrated approach, which includes the following steps:

- collection of the available scientific and technical data about the sites;
- sampling of earth materials (waste-rocks and soils) and plants;

- physical and chemical analyses of earth materials;
- chemical analyses of plant tissues;
- data processing (statistical and geostatistical analyses).

3.2 Geochemical characterisation of earth materials

3.2.1 Historical data

Besides the routine bibliographic research about the mine lands under investigation, also a historical data research was accomplished. The main purpose of this research was to find topographical maps reproducing the different physiography of the lands, to have useful information about the location of the excavation and of the disposal area to plan the following investigations. Moreover sketch maps of the mining work and annual reports about the mining activity were considered useful to integrate the preliminary data.

The problems related to the collection of historical data about abandoned mine lands are that not all the mine lands have a historical archive and a well-known historical archive is available, this rarely contain all the data or the data are in disorder. However, the time dedicated to search historical data is a little loss in the worst case, while it is a great improvement in the best case.

3.2.2 Sampling

A grid sampling was selected to a preliminary collection of earth material samples. This strategy allows an uniform coverage of the area, it is easy to use and also enables the estimation of spatial correlations, the identification of patterns and the increase in size of samples (US EPA, 2002). The choice between a central aligned square and an unaligned grid was only related to the mine lands logistic.

Planned samples were collected at 0.25-0.50 m depth, after removing the superficial part. They were put into a plastic bag and labelled. At the same time, two pictures, one of the sample site and one of the collected samples, were made and a preliminary description of the samples was done following, which contains the main measures and field observations. In table 3.1 the field card used during sampling procedures is shown.

EARTH MATERIAL - MINE LAND:			
Sample identifier:		Sampler:	
Date:			
Geographic coordinates:			
X (GPS):		Sketch map of location:	
Y (GPS):			
Z (pressure altimeter):			
Physical features:			
Nature of earth material:			
☐ Tailings	☐ Waste rocks	☐ Soil	
Grain size:			
☐ Cobbles	☐ Gravel	☐ Sand	☐ Silt and mud
Moisture:			
☐ Wet	☐ Humid	☐ Dry	
Vegetation:			
☐ Wood	☐ Brushwood	☐ Meadow	☐ Absent
Pictures:			
Sampling site:		Sample:	

Table 3.1: Field card for identification and description of earth materials.

3.2.3 Grain-size analyses

The particle size distribution was obtained by dry sieving. Since earth materials are often characterised by coarse fractions, the analysis was split into two steps: the first step *in situ* and the second step in laboratory. This allowed to work with a representative quantity of earth materials.

The first part of the analysis was conducted *in situ*, by separating the fractions >20 mm, 20-12 mm, 12-4 mm and <4 mm. This work was performed by hand, using sieves built on purpose. After this analysis about 2 kg of <4 mm fraction was sampled and brought to laboratory, where the second step of grain size analysis was conduced. Fractions of 4-2 mm, 2-1 mm, 1-0.5 mm, 0.5-0.025 mm, 0.25-0.125 mm, 0.125-0.0625 mm and <0.0625 mm were separated by dry sieving with a Controls D411 Automatic Sieve Shaker.

3.2.4 Colour analyses

The colour of waste rocks was determined *in situ* according to the Munsell® Color Soil Charts. The aim is to evaluate, according to Azzali et al. (2011), if any relationship could be established between soil color and mineralogical composition to plan a future survey campaign. As a matter of facts, the color variations (hue) of the samples are strongly affected by the presence of Fe-oxides and oxyhydroxides with goethite controlling the yellow hue (Y) and hematite the red hue (R) (Fernandez & Schulze, 1992; Scheinost & Schwertmann, 1999; Azzali et al., 2011).

3.2.5 Electrical Conductivity and pH values

Samples Electrical Conductivity (EC) and pH values were determined by equilibrating soils or earth materials in deionised water for 12 –16 hours (or overnight), at a solid to water ratio of 1:2.5 (w/w). They are considered as a screening tool, because pH value gives an indication of the inherent acidity of the waste material when initially exposed in a waste emplacement area.

3.2.6 X-ray fluorescence (XRF)

Earth material fraction <2mm were ground in an agate mill to a fine powder for subsequent geochemical analyses. Rock-forming elements and S_{tot} composition for each sample were determined by XRF analysis on powder discs using an automated Philips PW 1400 spectrometer.

Since the geochemistry of samples varies greatly, the XRF calibration straight line for rock-forming elements was built using a suitable set of standard materials. On the other hand, since the peculiarity of the environmental matrix, the XRF calibration straight line for total sulphur was built using different samples of S-rich mine dumps previously analysed.

3.2.7 Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)

Trace element concentrations were determined by ICP-AES (Jobin Yvon JY24) on solutions obtained by acid digestion (0.25 g powder leached with 6 ml 30% HCl Suprapure and 2 ml 65% HNO_3 Suprapure) in a closed microwave oven (Milestone 1200 Mega). All the element concentrations were determined directly in solution, with the exception of As that was measured using the hydride method. Calibration for this element was done with the standard addition method.

The analyses were performed in two phases, following the usual analytical procedures. In the first step, selected samples were analysed for 25 elements: Ag, As, Au, B, Ba, Bi, Cd, Co, Cr, Cu, Ga, Hg, La, Mo, Ni, Pb, Sb, Sc, Se, Sr, Th, U, V, W and Zn. In the second step, the trace elements that: (1) had shown the highest variability; (2) are known to be toxic; and (3) have a geo-environmental meaning were selected for further analyses on the whole samples collected.

Element concentrations were measured in triplicate and the percentage coefficients of relative standard deviation were below 10%, reaching maximum values of about 25% only for those concentrations close to the detection limit of the element.

3.2.8 Comparison with mineralogical data

The comparison between geochemical and mineralogical data set gives useful informations to better understand the main factors that controlled AMD processes (Frau & Marescotti, 2011 and references therein).

In order to identify the role of minerals in AMD processes, the following five classes can be distinguished by means of X-ray powder diffraction (XRPD) and optical (transmitted- and reflected-light) microscopy: (1) primary silicates; (2) primary carbonates; (3) primary sulphides; (4) other, subordinate, primary mineral species; and (5) secondary authigenic minerals.

The classes 1 through 4 represent the minerals that can have an active role in the AMD processes as reagents. In particular, the sulphide and carbonate classes have a major role in triggering and neutralizing water acidification, respectively. The other primary minerals can have either a passive role in the AMD processes, or can represent an additional source for the release of several PTE. Class 5 represent the reaction products formed from AMD solutions or replacing primary minerals during the oxidation processes. They often represent the intermediate step between the PTE-bearing primary minerals and the release of PTE to the environment because they can temporarily or permanently store contaminants through adsorption, coprecipitation or structural incorporation. They can also become a secondary source of pollution due to mineral breakdown and to the variation of physico-chemical parameters controlling sorption equilibria at the mineral–water interface.

3.2.9 AMD evaluation

As mentioned above AMD processes are the main cause of environmental pollution related to AML. The development of AMD processes begins when earthen material containing sulphides reacts with water in oxidant conditions. For this reason the evaluation of AMD potential of earthen material is of primary importance. At the present time two methodologies are available for the evaluation of this parameter and are classified as "static tests" and "kinetic tests".

Static tests

Static tests are a methodology based on the following two steps:

- the calculation of sulphuric acid that the earthen materials can produce starting from the analytic determination of their S content and the stoichiometry of the Eq. 4 reaction, shown in chapter one;
- the calculation of sulphuric acid that the earth materials can neutralize starting from titration tests.

After the analytic determination of S content of the earth materials, it is usually assumed that: (1) all the S is in the form of sulphide; (2) all the sulphide is in the form of pyrite; and (3) the Eq. 4 reaction is quantitative. The results are expressed in H_2SO_4/t that the earth materials can produce and the samples are plotted in a binary diagram and are grouped into 3 classes, according to Soregaroli & Lawrence (1997) :

1. AMD possible but not persisting in time due to low S content;
2. AMD possible and persisting in time due to high S content;
3. AMD impossible.

The AMD evaluation of earth material samples was made by the application of the AMIRA procedure (IWRI & EGI, 2002), which is a revision of the Sobek procedure (Sobek, 1978). The Acid-Base Account values refers to numerical data used to predict acid generation and they are calculated by the application of the following three components.

- *Determination of Maximum Potential Acidity (MPA)*

MPA is an estimate of the amount of acid that the sample can release by complete oxidation of sulphides, expressed as kg H_2SO_4/t (MPA value in kg H_2SO_4/t = wt.%S x 30.625). This evaluation is based on the conservative assumption that all S is present as pyrite. This simplification may overestimate the AMD as other sulphides with higher Me/S ratio have lower acid generation potential than pyrite. Moreover, such an overestimation can give marked and unrealistic results where high portions of S are present as non-acid generating phases (i.e. sulphates).

- *Determination of the Acid Neutralising Capacity (ANC)*

ANC is an estimate of the buffering capacity of the sample expressed as kg H_2SO_4/t that the sample is able to neutralise. It was experimentally determined by titration preceded by a "fizz test", as described by Sobek et al. (1978). When a negative value of ANC is obtained, it is reported in as 0.00, indicating the sample incapacity of neutralisation.

- *Calculation of the Net Acid Producing Potential (NAPP)*

The difference between MPA and ANC is referred to as the Net Acid Producing Potential (NAPP). NAPP is a theoretical value commonly used to indicate if earth material has potential to generate AMD. This value is also expressed in units of kg H_2SO_4/t and when is negative it indicates that the sample may have sufficient ANC to prevent acid generation. Conversely, positive value of NAPP indicates that the analysed material could be acid generating.

Alternatively, the ratio MPA/ANC, known as the Neutralisation Potential Ratio (NPR), can be used to evaluate the capacity of a material to generate AMD. Theoretically, a ratio < 1 implies that the sample could lead to acidic conditions, while ratio > 1 is indicative that the sample will not produce acid upon weathering. In practice, a safety factor is often applied and rocks with NPR greater than 2.3 or 4 are non-acid generating, whereas samples with NPR less than 1 have a likely acidification potential (Prince et al., 1997).

Kinetic tests

An important tool for geochemical assessment of mine areas are kinetic tests, as they provide an insight into the behaviour of the waste-rocks during the interaction with meteoric waters. Moreover, they give useful indications of metal mobility and chemical composition of the run-off waters by the reproduction of the natural processes in laboratory.

These tests consist in the leaching of a known quantity of earth material by a known quantity of water. The result is a coming out water that represents a surrogate of the surface or ground waters that pass through the mine dumps. The advantage of this methodology is the possibility to obtain direct information about the chemical and the physical properties of the drainage waters. Conversely, these tests could need a long execution time and it is very difficult to reproduce the real weather conditions.

A simple, cost effective, quick and qualitative leaching test was chosen (modified EPA Method 1312 SPLP, 1994) from the available pertinent literature. This kinetic test also provides indications of the potential chemical composition of run-off from the weathered surface of waste rocks. Slightly acidified de-ionized water, used for simulated natural precipitations, interacted in a rotary agitator for 18 hours with the < 2 mm fraction of the sample, at a solid to water ratio 1:20 (w/w). Total trace elements content of filtered solution were analyzed by ICP-AES, while a little aliquot of the unfiltered leachate was taken for pH, Electrical Conductivity and sulphate content analyses.

3.2.10 Statistical and geostatistical analyses

Major element concentrations, heavy metal contents and AMD values were processed by means of statistical and geostatistical methods in all the investigated area.

At first, an univariate descriptive analysis of chemical data was performed to describe the populations of the data and to identify outlier values. A geostatistical analyses was also carried out. Geostatistics was based on the theory of a regionalized variable (Matheron, 1963), which is distributed in space (with spatial coordinates) and shows spatial autocorrelation, such that the samples close together in space are more alike than those that are further apart. The geostatistical approach uses the technique of variogram (or semi-variogram) to measure the spatial variability of a regionalized variable, and provides the input parameters for the spatial interpolation of kriging (Webster & Oliver, 2001). This method allows the evaluation and the spatial limitation of areas belonging to the different classes, characterised by the same values of PTE contents or AMD parameters.

3.3 Biogeochemical characterisation of wild flora

3.3.1 Bibliographic research

After identifying the pioneer species growing on waste-rock dumps, a bibliographic research about their physiology and ecology is useful to understand their survival strategies at mine lands. Only the most interesting species can be then collected and analysed, in order to: (1) study their metal tolerance strategies; (2) identify species suitable for phytoremediation projects; and (3) understand how PTE could move through food webs.

3.3.2 Sampling

Plants grow with an irregular distribution on waste-rock dumps and tailings: for this reason it is not possible to collect samples according to a regular grid. A significant amount of plant aboveground and underground tissues were then randomly collected in the same substrate sampling places, at a maximum distance of about 3-4 meters from the exact point of the earth material sampling. For each sampling point, many specimen (up to 6-7) were collected and; for each specimen an amount of 50 g of leaves and 200-300 g of branches and roots tissues (wet material, WM) were collected.

In table 3.2 the field card used during vegetation sampling procedures is shown.

VEGETATION - MINE LAND:	
Sample identifier:	Sampler:
Date:	
Geographic coordinates:	
X (GPS):	Sketch map of location:
Y (GPS):	
Z (pressure altimeter):	
Plant species:	
Plant tissues: ☐ aboveground (☐ leaves ☐ branches) ☐ underground	
Age: ☐ < 1 year ☐ 1 – 3 years ☐ 3 - 5 years ☐ 5 - 10 years ☐ > 10 years	
Distance from earth material sample:	
Nature of earth material: ☐ Tailings ☐ Waste rocks ☐ Soil	
Pictures:	
Sampling site:	Sample:

Table 3.2 Field card for identification and description of vegetation.

The time of the year when sampling is done is also an important parameter to evaluate. In the early autumn metal accumulation in tree leaves is supposed to be highest as the loss of autumn leaves cold be a detoxification strategy that deciduous accumulator plant species could adopt to remove PTE from their tissues (Pulford and Watson and references therein, 2000).

3.3.3 Chemical analyses

In the laboratory the plant material was first washed thoroughly with tap water, to remove any soil particles attached to their tissues, and then was cleaned with distilled water. After that, samples were dried in an oven at 60°C, homogenized and finally powdered with an electric crusher to reduce and homogenized size. For PTE analysis, plant samples were digested in a 7 ml 65% HNO_3 Merck Suprapur and 3 ml 30% H_2O_2 Merck Suprapur mixture in a closed microwave oven (Milestone 1200 Mega) and they were then accurately filtered and diluted with Milli-Q water before the analysis. Also in this case, all the PTE concentrations were determined by ICP-AES (Jobin Yvon JY24) directly in solution, with the exception of As that was measured using the hydride method. Calibration for this element was done with the standard addition method. Element concentrations were measured in triplicate and the percentage coefficients of relative standard deviation were below 10%, reaching maximum values of about 25% only for those concentrations close to the detection limit of the element.

3.3.4 Identification of metal tolerance strategies

The identification of strategies of tolerance is carried out by the calculation of two important bio-geochemical parameters: (1) Bioaccumulation Factor (BF); and (2) Translocation Factor. By comparing these two parameters we can define the ability of different plants to take up metals from the substrate and transport them to the shoots or stabilize and immobilize them in soils.

Bioaccumulation Factor (BF) is defined as the ratio between the trace-element concentration in the plant biomass and the one into the soil (dry material, DM). Its value is usually > 1 in accumulators and < 1 in excluders, while hyper-accumulators also show BF values >> 1 (McGrath & Zao, 2003). Moreover, Translocation Factor (TF) indicates preferential partitioning of metals inside plant tissues, as is defined as the ratio of metal concentration in the leave tissues (DM) to that in roots (McGrath & Zao, 2003). Accumulators species generally transport PTE from their roots to the apical parts, as they are able to survive despite high internal toxic element concentrations; for this reason their TF values are >1. On the other hand, excluder species generally retain PTE inside root tissues to avoid their transport to leaves. Where metal toxicity would occurs, TF values are then <1.

Chapter 4

Application 1:
Rosia Montana mining area (Romania)

Rosia Montana is a hydrothermal gold deposit, exploited since Roman times. It is located within the gold District known as the gold Quadrilater, which constitutes the biggest gold reserve in Europe.

Exploitation occurred at large scale mainly in gallery during 19th and beginning of 20th century under Austrian Empire. In the last 60 years exploitation was made by a state-owned mining company and developed mainly in open pit; by 2005 exploitation was reduced to minor extraction from one open pit and at the moment no exploitation occurs. Reserves are estimated to 300 t gold and 1000 t silver and mining licence was acquired by a private mining company: big exploitation plans with opening of four large open pits are on the way.

As a matter of facts, century of exploitation caused a significant environmental damage and the excavation and exploitation of tunnels and open pits has generated a large amount of waste-rocks dumps, some of them located close to villages. Moreover, strong pollution from this mine with huge AMD problems has already been assessed and documented in several scientific works (e.g. Florea et al., 2005 and reference therein). It is due to porphyric texture of host rock, strongly disseminated mineralization, very rich and large paragenesis (huge amount of pyrite, other base metal sulphides, silver sulphosalts and gold), huge gallery and open pit works. Private company provided remediation plans for the past mining activity and mitigation plans for reopening.

This mine sites was chosen for the application of different biogeochemical analytical methodologies, since a wide geological, hydrogeological and environmental data base is available and mine exploitation development has been planned, so it was possible to select a specific area to apply the method developed to predict possible consequences of specific planned actions.

4.1 Site overview

Rosia Montana (N46.29694, E23.12063) is located at an altitude between 770 and 920 m a.s.l. in the Alba county, 16 km East of the town of Campeni and 128 km South-West from Cluj Napoca, the main Transylvanian town. This mining area is part of the historic gold mining area of about 550 km^2, known as "The Golden Quadrilateral" and located in the Apuseni Mountains of Transylvania, as shown in Figures 4.1a and 4.1b.

Fig. 4.1 a: location of the Romania country.

Fig. 4.1 b location of the Golden Quadrilateral Region in Romania.

4.1.1 Geological features

Rosia Montana mininig area is located in the southern portion of the Apuseni Mountains, where the following geological formations outcrop (see Figure 4.2).

- Flysch (Cretaceous), consisting of carbonaceous marls, shales and turbidite sequences composed of siltstones and conglomerates; it constitutes the local basement of the magmatic rocks.
- Volcaniclastic breccia (Miocene) consisting of coarse polygenic-metamorphic rocks, dacite and andesite ± flysch-matrix supported breccia.
- Montana dacite (Miocene), that occurs in the form of two intrusive domes and volcaniclastic breccias and is characterised by the primary magmatic minerals, except quartz phenocrysts, partially to completely replaced by secondary minerals. Kouzmanov et al. (2005) have dated zircons at 13.61 ± 0.07 Ma with the U–Pb method.
- Rotunda andesite (Miocene), that is present as intrusive domes emplaced at shallow depth, thick lava flows and pyroclastic breccias. It covers both the Cretaceous flysch and the Miocene igneous

rocks along a subhorizontal contact. Roşu et al. (1997, 2004) have dated the andesite 9.3 ± 0.5 Ma

- with K–Ar method.
- Breccia (Miocene) consisting of clasts of shales and altered dacite (Manske et al., 2006).

Rosia Montans was first described as an epithermal low sulfidation deposit (Marza et al., 1997), due to the typical adularia and sericite alteration and to the abundance of carbonates. Later, epithermal Au–Ag ores of the Apuseni Mountains were described as low- to intermediate-sulfidation deposits (Alderton & Fallick, 2000) and finally as intermediate-sulfidation deposits (Manske et al., 2006; Wallier et al., 2006).

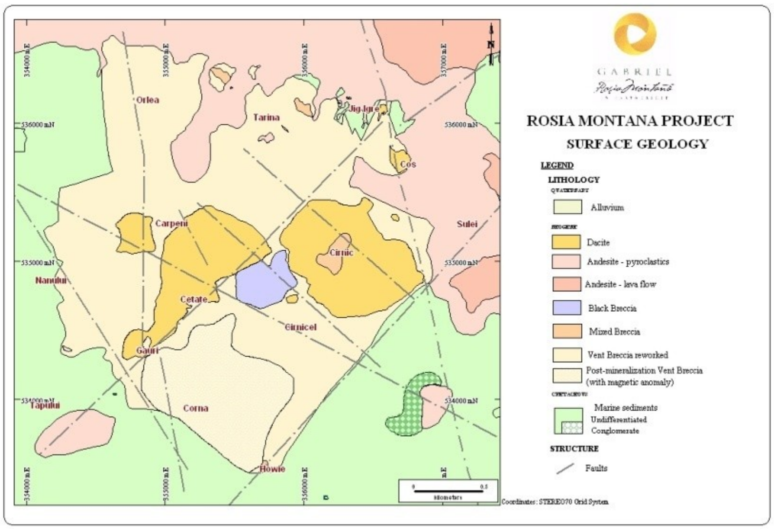


Fig. 4.2: Rosia Montana geological features.

Hydrothermal adularia alteration with a phyllic overprint is pervasive and ubiquitous, whereas silicification, argillic alteration and chlorite-calcite alteration occur locally (Wallier et al., 2006).

The Rosia Montansa deposit is mainly hosted by two bodies of dacite called Carnic and Cetate Hills, whose morphology is now reversed due to open pit mining; moreover, it is strictly associated with a pipelike breccia body emplaced during phreatomagmatic activity (Wallier et al., 2006). Mineralisation and associated alteration involved also the dacite bodies, the volcaniclastic breccias and the surrounding Cretaceous sedimentary rocks (Manske et al., 2006). Deep silicification is widespread within the Cetate Hill, argillic alteration can be found to the North and South- East of Cetate Hill and chlorite-calcite alteration is present only to the North-East of Carnic Hill. Mineralizations consist of native gold, pyrite, sphalerite, galena, chalcopyrite, tetrahedrite in a quartz ± adularia ± carbonates gangue and occur either as disseminations or veins and vugs filling.

4.1.2 Climatic features

The analysed data were collected from the Rotunda meteorological station, 2 km northward from the Rosia Montana mine and concern the most recent data set, collected from 1982 to 2005.

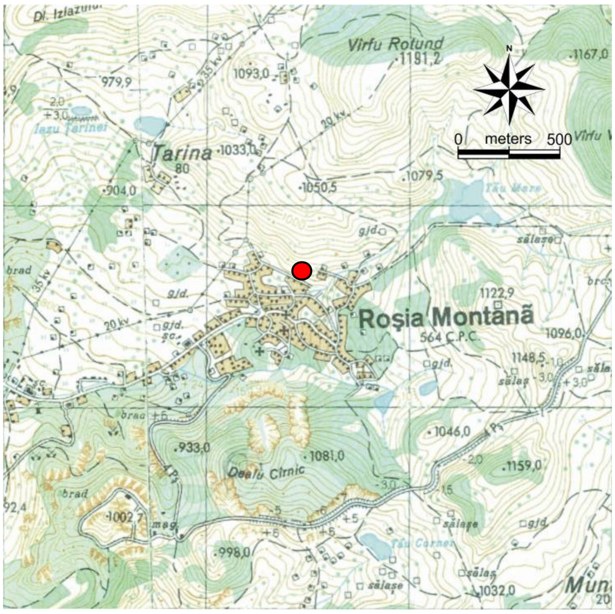


Fig. 4.3: Localisation of Rotunda meteorological station (from the original topographic cart, 1979, 1:25,000)

The mean annual rainfall is 739 mm, with a minimum between November and February and a peak in July. In addition to rainfall, the average snowfall is 64 cm/y, equivalent to about 64 mm/y of rain, that, added to the rainy precipitations, gives a total of 803 mm/y.

The average annual temperature is 5.7 C, with a minimum in January (-4.7 C) and a maximum in August (16.9 C).

4.1.3 Hydrological features

Rosia Montana mining district is located near the headwaters of Corna, Saliste and Rosia streams, all flowing towards Abrud River, a tributary of Aries River. Corna Valley watershed drains South-West towards Abrud River just upstream of both Abrud and Saliste towns; Rosia Valley watersheds flow west to Abrud River further downstream.

This area is characterised by moderately steep mountainous terrain ranging from 700 to 1,000 meters a.s.l. The main source of groundwater recharge at the mine site is rainwater. The streams gain groundwater as the result of the low-permeability of the geologic units and convergent groundwater flow. The average flow rates for Rosia Valley, Corna Valley and Saliste Valley streams for the period 2001–2003 were 0.16, 0.07 and 0.16 m^3/s, respectively (RMGC, 2006).

Rosia Valley collects waters from the underground network of tunnels, all hydraulically connected. They act as drain channels for the upper part of the valley and discharge to the surface in a point located at an elevation of 714.6 m (i.e., at the adit of the "Sf. Cruci din Orlea" gallery, shown in the figure 4.4a). Waste-draining waters are, in this valley, the main contamination sources of Rosia stream, displaying both a strongly acidic character (pH values between 2.68 and 3.03) and elevated contents of As, Cd, Ni, Al, Cr, Se and SO_4^{2-} (Bird et al., 2005; RMGC, 2006).

Owing to the high flow rate of mine waters and to the naturally low flow rate of Rosia stream, the dilution factor is low, thus leading to the contamination of the waters downstream the discharge points (Florea et al. 2005). These watercourses comprise a portion of the Aries watershed and the tributary headwaters that form a part of the hydrographic Danube Basin.

Fig. 4.4.: adit of the "Sf. Cruci din Orlea" gallery

Fig. 4.5: confluence of Abrud river (on the left), which collects mine waters from the Rosia Montana mine area, and Aries river (on the right).

4.1.4 Mining history

The earliest reference to the town of Rosia Montana is on a wax tablet dated February 6th 131 A.D. Archaeological excavations have led to the discovery of old houses, cemeteries, tunnels and miner's tools, as well as 25 wax tablets that bear inscriptions in Greek and Latin. The Romans left Dacia in 271 A.D. and there are reports of a resumption of mining in the middle Ages, by German immigrants who used techniques similar to those of the Romans.

A significant development of the mining took place under the Austro-Hungarian Empire and, after its fall in 1918, mining continued in the form of small grants of limited size allocated to local citizens until 1948, when the gold mines were nationalized. In 1971 a large open pit was opened on the Cetate hill soon followed by a second one on the Carnic hill. The mine was conducted by Rosiamin, a subsidiary of state-owned Regia Autonoma a Cuprului Deva (RACD). The extracted ore was enriched by flotation in a facility located in Gura Rosiei; afterwards gold was extracted with a process that involved the use of cyanide in another plant located in Baia de Aries.

Underground mining continued until 1985 when, following a major collapse of a tunnel and the dramatic death of several miners, the underground exploitation was abandoned and only the open-pit mining was continued to be used.

The enormous environmental damage caused by centuries of exploitation alerted the public and in particular the environmental community. In 2000, the European Union (EU) put the closure of mining activities, followed by reclamation and environmental restoration as a condition for Romania joining the EU. The mining claim (approximately 62 km^2) was then transferred from Minvest SA Deva, the heir of the RACD, to the Rosia Montana Gold Corporation (RMGC). Rosia Montana Gold Corporation is now working on the mining area, in agreement with the EU, at its own expenses to clean the area and with the goal, to resume fruitful and environmentally sustainable mining activities after remediation.

As a matter of facts, the excavation and exploitation of tunnels and open pits has generated a large amount of waste-rocks dumps, some of them located close to villages. Moreover, the area is characterized by extensive AMD processes and heavy metal contamination, which affect also the surrounding streams (Florea et al., 2005). The ARD potential of the waste rocks in all Rosia Montana area was determined both by static and kynetic procedures (RGMC, 2006) and more recently by a field-based kynetic testing (Costin et al., 2011).

4.1.5 Mining activity

Currently, the Rosia Montana mine is characterised by the presence of two open pits called Cetate and Carnic (163×10^6 and 227×10^6 tons of material exploited, respectively); in addition, there are more than 100 km of underground tunnels, spread on several adits and on a vertical span of 300 m. Cetate open pit is shown in figure 4.6. Mining wastes and tailings are piled up on-site (about 256×10^6 tons of mining-waste material), into two main waste-rock dumps (Hop and Valea Verde), several minor deposits and two tailing stockpiles (see fig. 4.7).Acid sulphate waters (with pH values as low as 3) that continuously flow out from the lowest gallery ("Sf. Cruci din Orlea"; 714 m a.s.l.), very close to the confluence with the Rosia River, indirectly testify that the AMD processes are still active and intense in the whole mining area.

Fig. 4.6: Cetate open pit.

Fig. 4.7 a: waste-rock dumps surrounding Cetate open pit.

Fig. 4.7 b and c: waste-rock dumps surrounding Cetate open pit.

4.2 Hop waste-rock dump earth material characterisation

4.2.1 Hop-waste rock dump

Hop waste-rock dump was piled up between 1998 and 2000 and it has a horse-shoe shape, with a maximum thickness of 38 m. The highest part is flat, with a surface of 18,000 m^2 and the top is 920 meters a.s.l. It is composed of waste rocks deriving from the excavations of the adjacent Cetate open pit. A portion of this dump was chosen for geochemical characterisation, because:

- is a plain easily-accessible area;
- the heterogenity of waste-rocks is well represented.

A rectangular area on the eastern Hop waste-rock dump was then chosen and a 25-m^2 grid was designed for sampling. This area was further divided into square cells to form a sampling grid where 25 composite earth material samples (about 2 kg) were collected, as shown in figure 4.10. Despite only a limited area was sampled, it can be considered representative also for statistical analysis, because all the material comes from the Cetate open pit and is made by andesitic breccia and dacite.

The 25 collected samples were analysed by relative guideline procedures and then interpolated by geostatistical elaboration. Results are shown in Appendix A.

Fig. 4.8 a: panoramic view of the Hop waste-rock. The red box represents the sampling area.

Fig. 4.9: panoramic view of the sampling area.

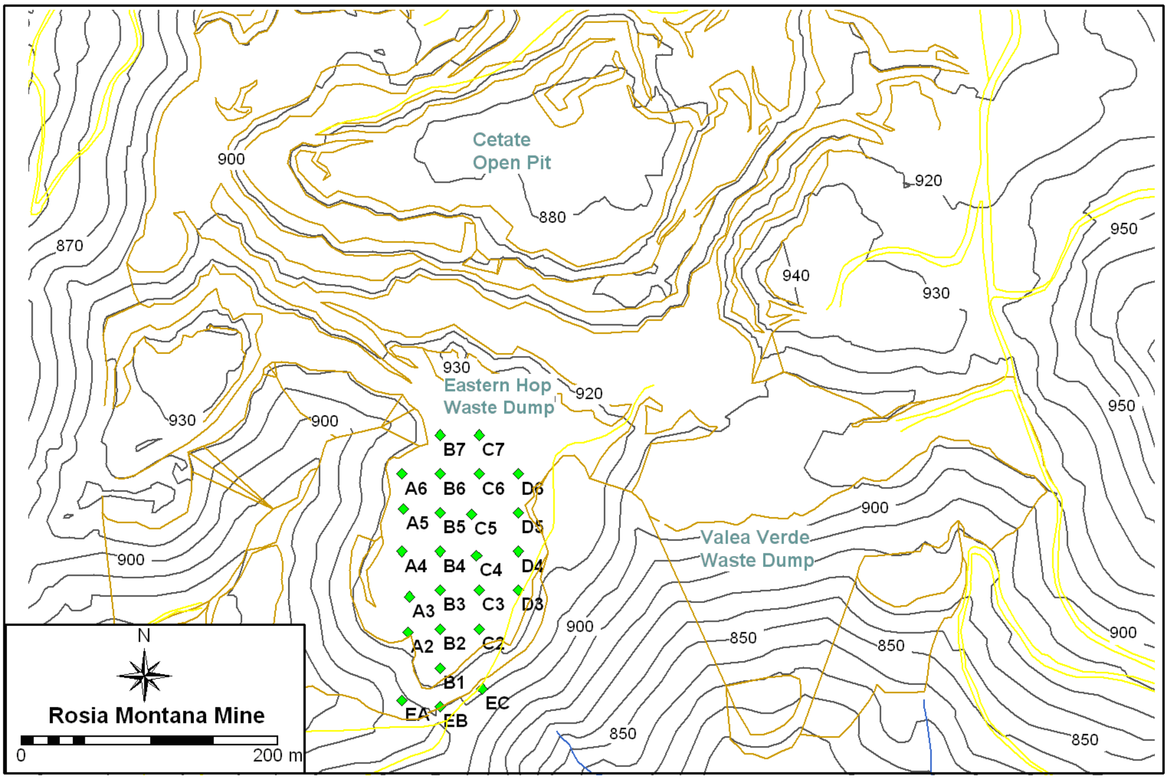


Fig. 4.10: localisation of the Hop waste-rock dump and the sampling grid (1); Valea Verde waste-rock dump (2); and Cetate open pit (3).

4.2.2 Grain-size

The grain size analysis is useful to understand the percentage of reactive material and the relationships between the grain size and the chemical processes, investigated by means of kinetic test.

As shown in figure 4.11, all the waste rock samples can be classified as sandy gravel or as gravely sand (Blott & Pye, 2001). Particle size distribution data are presented numerically (Appendix A.1) using cumulative coefficients. In particular:

- the measure of central tendency (D50) ranges from 879.1 to 5248.8;
- the a measure of distribution width (D90/D10) ranges from 15.95 to 174.78.

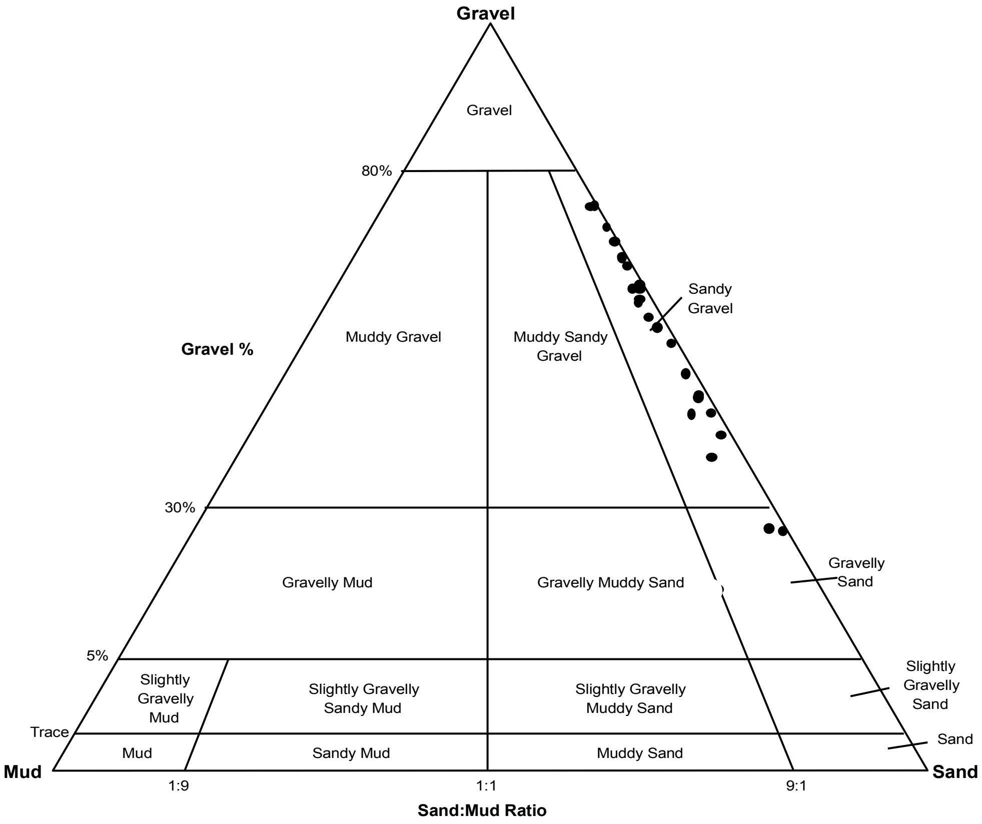


Figure 4.11: grain-size classification of wast rocks coming from Hop waste-rock dump.

4.2.3 Colour and screening tool (EC and pH)

The colour hue, value and chroma are reported in Appendix A.1. According to Munsell® Color Soil Chart, all waste rocks can be prevailingly classified in two groups, as 2.5Y and 10YR for hue parameter. A distinction between this two groups can be better performed on the basis of value and chroma parameters, since a first group of waste rocks has, on average, higher value and chroma parameters than a second group, which chroma parameter is always equal to one. The first group is called WR1, while the second is called WR2. Figure 4.13 shows the different colour of two samples belonging to the two different groups.

Results from screening tools analyses show that also pH values are quite different between the two WR groups: in particular WR1 group is characterised by lower values (mean = 4.0) than WR2 (mean = 7.8). On the other hand, EC values show a great variation in both groups, ranging from 111 to 2,550 µS/cm (see Appendix A.4).

Fig. 4.13: difference in colours of two sample belonging to WR1 group (on the left) and WR2 group (on the right).

4.2.4 Geochemistry

The chemical analysis of the major and trace elements was carried out to confirm and/or refine the distinction among the WR1 and WR2 groups of samples, as resulting from the colour and screening tools analysis.

These results show that WR1 group is characterized by a content of SiO_2 ranging between 56.58 and 63.80 wt %, whereas WR2 is characterized by a content of SiO_2 ranging between 50.04 and 52.88 wt % (see Appendix A.2).

Moreover, WR1 samples differ significantly from WR2 also for the contents of:

- Na_2O (0.13 ÷ 0.61 wt % vs. 1.12 ÷ 2.13 wt %);
- MgO (0.89 ÷ 1.80 wt % vs. 2.48 ÷ 4.22 wt %);
- CaO (0.01 ÷ 1.49 wt % vs. 4.59 ÷ 7.00 wt %)
- and K_2O (6.54 ÷ 8.91 wt % vs. 3.83 ÷ 6.04 wt %).

Figure 4.13 represents the different major element composition between the two WR groups.

The calculation of mean and variation range is shown in Table 4.1. Some samples (such as B2, B5 and C6) are excluded from these calculations, as they cannot be attributed surely to one of the two groups, probably because they are composed by a mixture of the two lithologies.

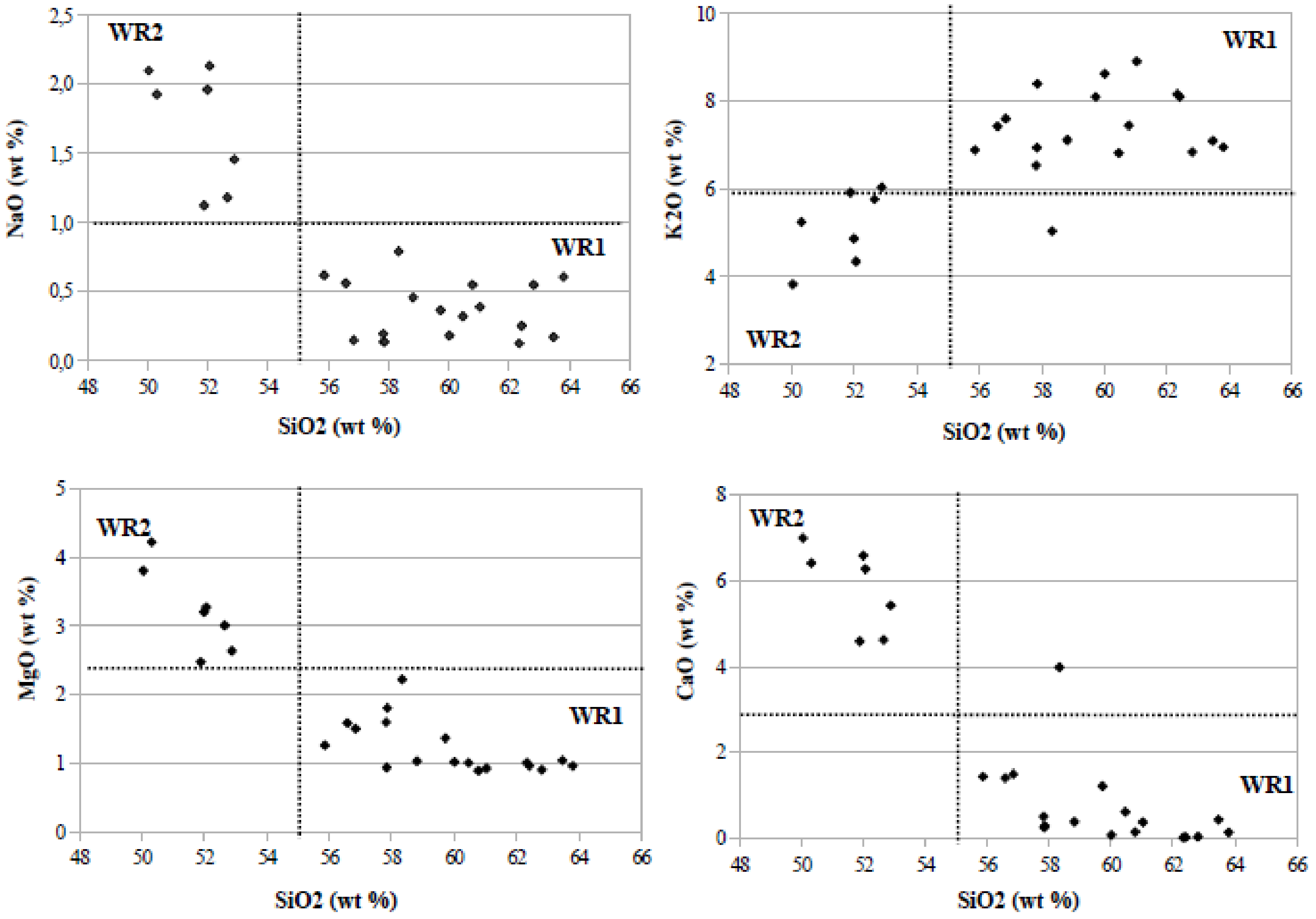


Fig. 4.13: chemical composition of earth material samples belonging to WR1 and WR2 group.

		Major elements %				
		SiO_2	Na_2O	MgO	CaO	K_2O
WR1	Mean value	60.19	0.32	1.14	0.41	7.53
	Variation range	56.58	0.13	0.89	0.01	6.54
		63.80	0.61	1.80	1.49	8.91
WR2	Mean value	51.69	1.70	3.23	5.85	5.15
	Variation range	50.04	1.12	2.48	4.59	3.83
		52.88	2.13	4.22	7.00	6.04

Table 4.1: significant major elements mean values and ranges of variation of the two waste rocks groups.

A set of PTE (Ag, As, Cu, Ni, Pb and Zn) was analysed according both to the geological characteristics of the area and the works carried out on site (see Appendix A.3). The results are summarized in Table 4.2, which shows the mean values and ranges of variation of Ag, As, Cu, Ni, Pb and Zn. WR1 group is characterised by a mean content of Ag (4.3 mg/kg), As (117.5 mg/kg) and Pb (42.5 mg/kg) higher than WR2 group, that shows mean concentrations of 1.7, 59.7 and 29.7 mg/kg, respectively. Conversely, WR2 group has a mean value of Cu (47.3 mg/kg), Ni (9.0 mg/kg) and Zn (108.1 mg/kg) higher than WR1 group (30.4, 3.4 and 48.3 mg/kg, respectively).

In general, the concentrations of PTE into the waste rocks are below the regulatory limits (Carlon, 2007), with the exception of As, which has concentrations up to 10 times higher than those prescribed by law.

		Potentially toxic trace elements (mg/kg)					
		Ag	As	Cu	Ni	Pb	Zn
WR1	Mean value	4.3	117.5	30.4	3.4	42.5	48.3
	Variation range	1.1 – 13.9	80.3 – 231.0	11.6 – 60.6	0.8 – 13.4	29.3 – 88.4	10.2 – 114.7
WR2	Mean value	1.7	59.7	47.3	9.0	29.7	108.1
	Variation range	0.0 – 5.7	46.7 – 88.2	39.9 – 54.8	8.1 – 12.4	22.2 – 36.1	72.7 – 204.4

Table 4.2: PTE mean values and ranges of variation of the two waste rocks groups.

The presence of two different WR groups well agree with previous studies (Alderton & Fallick, 2000), showing that the rocks outcropping at Cetate open pit are andesitic breccias and dacites. In Table 4.3 the analyses of two samples of andesitic rocks from a locality situated 30 –60 km southwest of Roşia Montană, are included for comparison. Although these rocks do not constitute samples of the same Cetate lithology, they are interesting because they show the change in composition from unaltered to altered and mineralized dacite and/or andesite.

	Major and trace elements (mean values)						
	CaO %	Na_2O %	K_2O %	Rb mg/kg	Sr mg/kg	V mg/kg	Zr mg/kg
WR1	0.41	0.32	7.53	278.4	60.9	100.0	178.2
WR2	5.85	1.70	5.15	187.9	118.0	161.0	203.4
94-25 fresch*	*6.53*	*3.37*	*1.24*	*1.7*	*533.0*	*141.0*	*104.0*
94-23 altered*	*1.26*	*0.03*	*5.07*	*253.0*	*29.0*	*139.0*	*95.0*

Table 4.3: Major and trace elements mean value of the two waste rocks groups, compared to data from Măgura (*Alderton & Fallick, 2000).

Due to the supergenic alteration that involved the waste rocks, all WR samples are depleted in CaO and Na_2O and enriched in K_2O compared to the parent material. Moreover, the pervasive supergenic alteration mobilizes Rb and Sr, with the result that the alteration products are Rb-enriched and Sr-depleted, compared with the parent rocks.

On the other hand, V and Zr are relatively immobile during alteration and the detected contents should be related to the different chemical composition of parental rocks. WR2 samples show an average V and Zr contents (161 and 203.4 mg/kg, respectively) higher than WR1 values (100 and 178.2 mg/kg, respectively). Since V and Zr behave as incompatible elements in magmatic systems, their distribution confirms that WR2 samples derive mainly from less differentiated rock as andesite, while WR1 can be associated with more differentiated dacite. A certain allocation of the two groups to igneous lithologies is however not likely, because:

- the parent material is altered and mineralized, so it may not exactly reflect the chemistry of a single magmatic rock types;
- the waste rocks are reprocessed materials that may not fit with the parent material;
- for this study only the fraction size < 2 mm was analysed, whereas there are evidences that composition slightly changes with grain size, in particular SiO_2,whose concentration increases with grain size increasing.

4.2.5 Comparison with mineralogical data

The mineralogy of the samples was determined by the collaboration of DISTAV – Dipartimento di Scienze della Terra, dell'Ambiente e della Vita (Università degli Studi di Genova) and the percentage of the different classes, calculated on the basis of their relative modal abundance, is shown in Appendix A.4.

On the basis of this mineral modal abundance estimations, the WR1 and WR2 samples resulted clearly different, in particular for the silicate, carbonate and sulphide contents. As a matter of facts, WR1 samples have higher silicate concentration than WR2 samples (65.4–84.5 % vs 59.1–65.8 %). Moreover, dacite clasts represent more than 60% of the silicate class and they are much more abundant respect to the andesites and the other lithotypes, which significantly increase in WR2 sample, where they can represent more than 80 % .

On the contrary, all WR2 samples contain much more carbonates than WR1 (14.7–24.5 % vs 0–10.2 %); in particular twelve of the seventeen WR1 samples do not contain carbonates at all. Sulphide content, represented mainly by pyrite, is highly variable among the two waste rock groups: the highest concentrations occur in the WR1 group, reaching the maximum value of 13.5 %. Finally, the secondary authigenic mineral content is highly variable, but very similar among the two groups (WR1:7.5–20.8 %, WR2: 10.2–13.2 %).

4.2.6 AMD evaluation by static tests

Acid mine drainage static test results (see Appendix A.4) show that on the eastern Hop mine dump the potential for AMD generation is widespread. Indeed, all the samples have S concentration higher than the detection limit of 0.01 wt %, reaching the highest concentration of 2.07 wt % in WR1 group and resulting that the MPA is between 0.31 kg H_2SO_4/t and 63.34 kg H_2SO_4/t.

As a result of MPA and ANC variability on a total of 25 samples, 15 have positive NAPP, 2 have NAPP around zero and 8 have negative NAPP. This different AMD behaviour can be explained by the differences in mineralogy and lithology.

As shown in fig. 4.14, following the Soregaroli and Lawrence (1977) classification:

- one sample falls in field I, which means that the AMD is possible but will not persist over time, due to the low S content;
- fifteen samples fall in field II, meaning that AMD is possible and persists over time, due to
- the high S content;
- one sample falls in the field III and eight samples are in the field IV, which means that the AMD is impossible.

At present, the waste rock dump is then a source of acid drainage. Fifteen of twenty-five samples have positive NAPP (an average value of 34 kg H_2SO_4/t), although the sulphur concentrations found are not so high if compared with other mining sites (Nordstrom et al., 2000; Morin & Hutt, 2001). In terms of AMD features, WR2 group has ANC > MPA, and therefore it is able to buffer the production of acidic water. On the other hand, WR1 group has always nil ANC and positive MPA, therefore it is a source of acid drainage.

Net acid producing potential versus S total (S_{tot}) chart shows that the two parameters are strongly correlated, but with an almost constant downward shift of WR1 group data of 80 kg H_2SO_4/t. Such kind of correlation indicates that NAPP changes within each group are correlated to S tot content. The constant Δ NAPP value between the two groups can be attributed to the presence of ANC phases in WR2 samples.

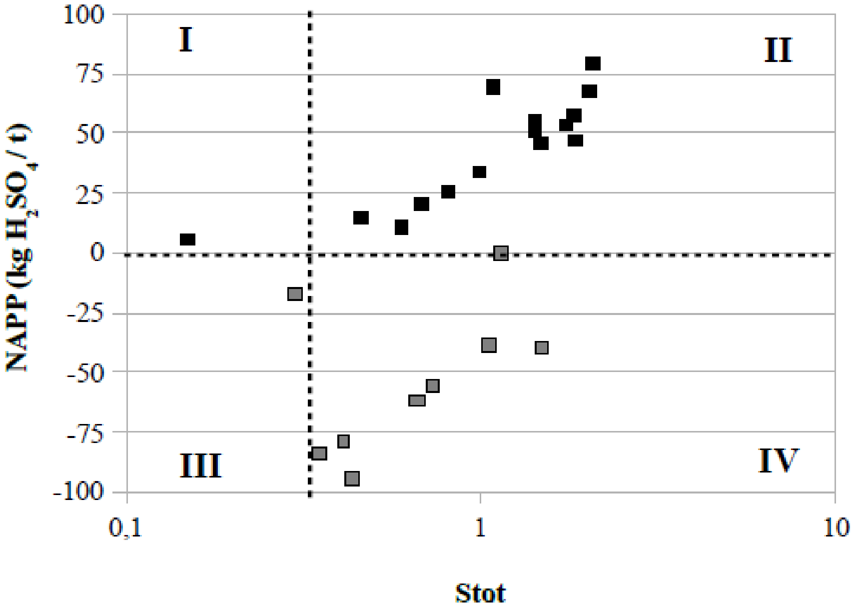


Fig. 4.14: relationship between NAPP values and S_{tot}

4.2.7 AMD evaluation by kinetic tests

The Modified EPA Method 1312 SPLP (1994) has been applied to seventeen of twenty-five samples and results regarding pH, EC values, sulphate content and selected PTE (Cu, Zn and As) concentration of the leached waters are shown in Appendix A.3.

The pH values of the leached waters vary greatly (from 3 to 9), according to mineralogical and geochemical composition of the waste materials. Leached waters originated by WR1 samples interaction have a pH mean value lower than waters that interacted with WR2 samples (3.7 vs 8.2).

The sulphate content is highly variable, ranging from 16.5 to 475 mg/kg and a significant positive relationship between sulphate concentration and EC was found, as shown in the Figure 4.15.

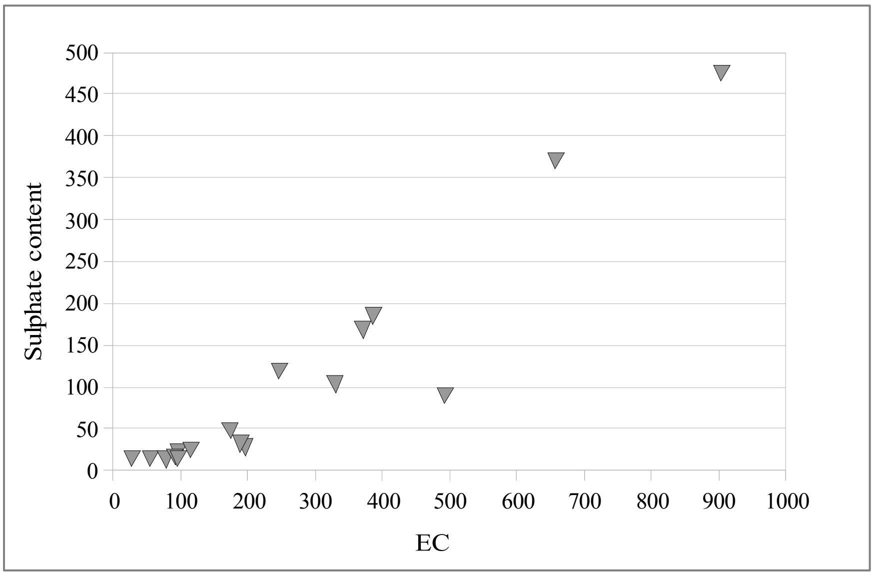


Fig. 4.15: relationship between EC (µS/cm) and SO_4^{2-} content (mg/kg) in leached waters.

Moreover, SPLP result showed that PTE content in filtered solution is generally low: Cu ranges from 0 to 98 µg/kg (mean 14), Zn ranges from 21 to 570 µg/kg (mean 155) and As ranges from 1 to 7 µg/kg (mean 2.5). These data are in agreement with the results of bulk waste-rock material chemical composition, whose metal concentrations are in the range of tens of mg/kg with the exception of As, that shows a content one order of magnitude higher.

4.2.8 Geostatistical elaboration

From an engineering point of view it is useful to know the spatial distribution of AMD variables and PTE concentrations on the whole area, so contour maps were made applying ordinary kriging interpolation on each variable, as shown in Figure 4.16 and 4.17. Variogram parameters are reported in Table 4.4.

All the following contour maps represent the U.T.M. coordinates of the sampling point and the minim and maximum value of each variable. These are usually shown in green and in red respectively, except for pH lower acid values that are shown in red. Moreover, since As is the only element whose concentrations reach hazardous levels, its spatial distribution on Hop waste-rock dump is represented with a different colour scale.

Variable	Model	Scale	Length	Anisotropy
pH	Exponential	5	3	1
NAPP	Exponential	900	2	1
Ag	Exponential	7	5.5	1
Cu	Exponential	70	2	1
Zn	Exponential	150	6	1
As	Exponential	600	5	1

Table 4.4: variogram parameters of the contour maps shown in figure 4.16 and 4.17.

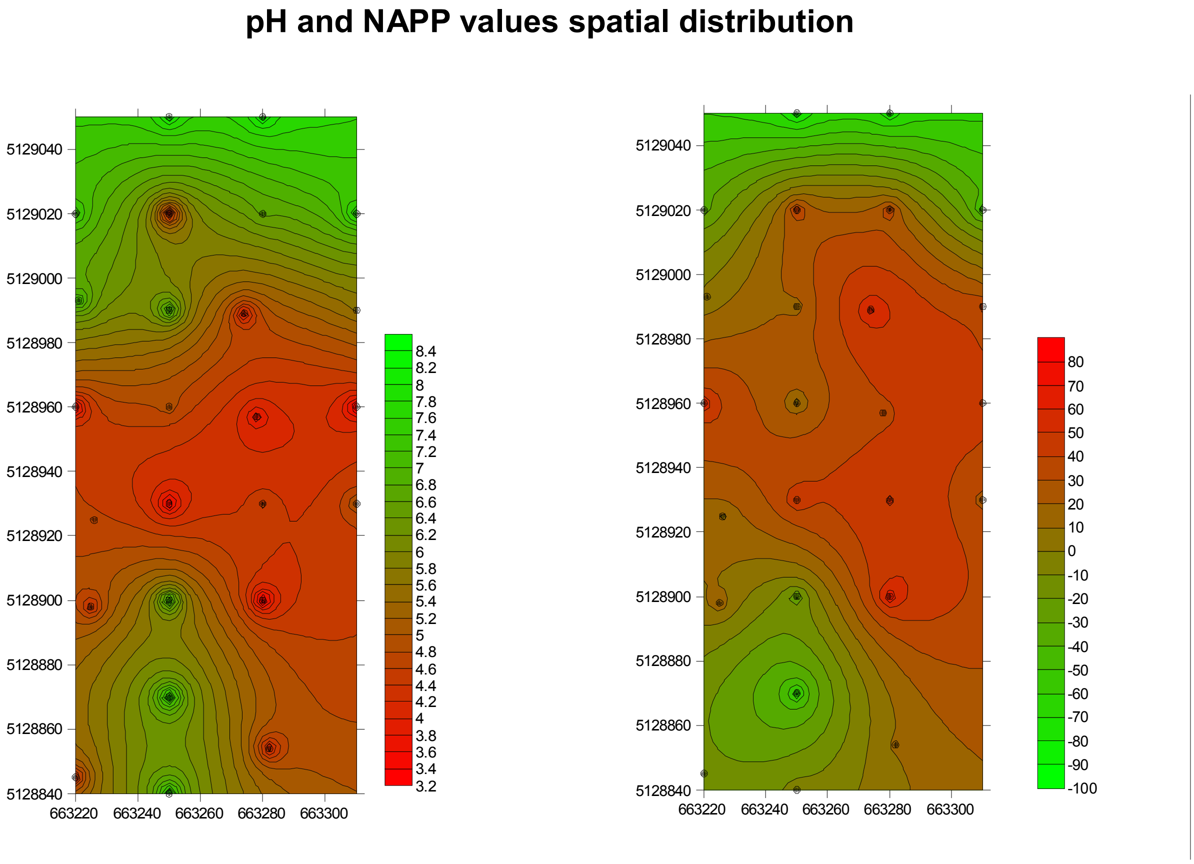
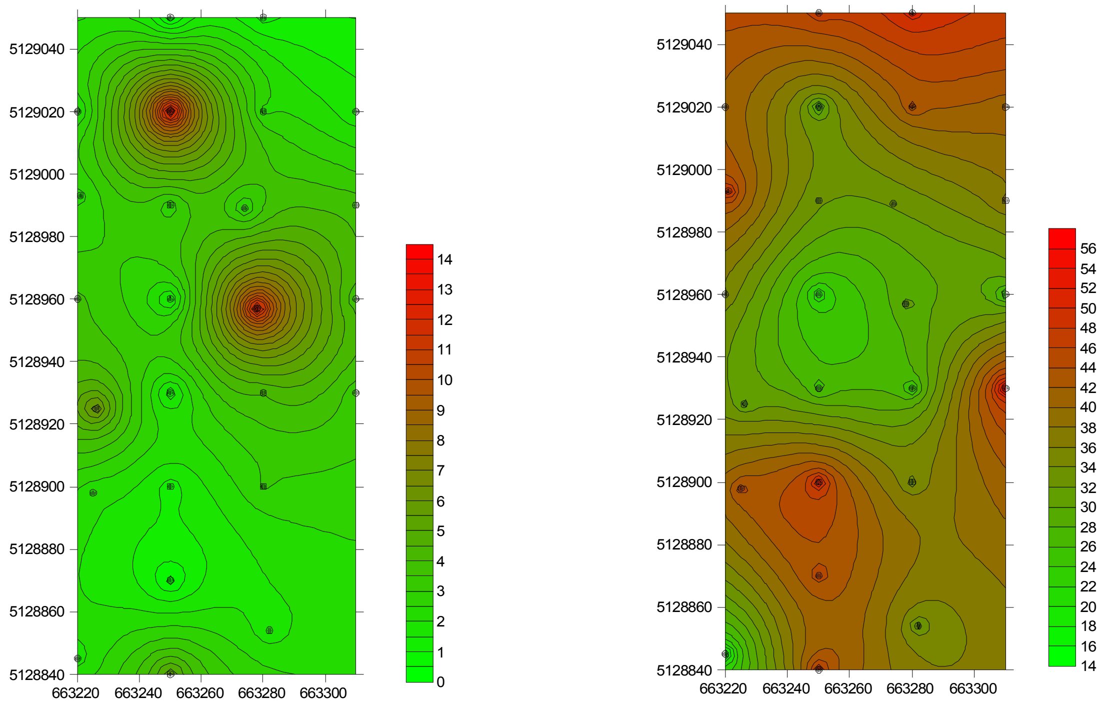
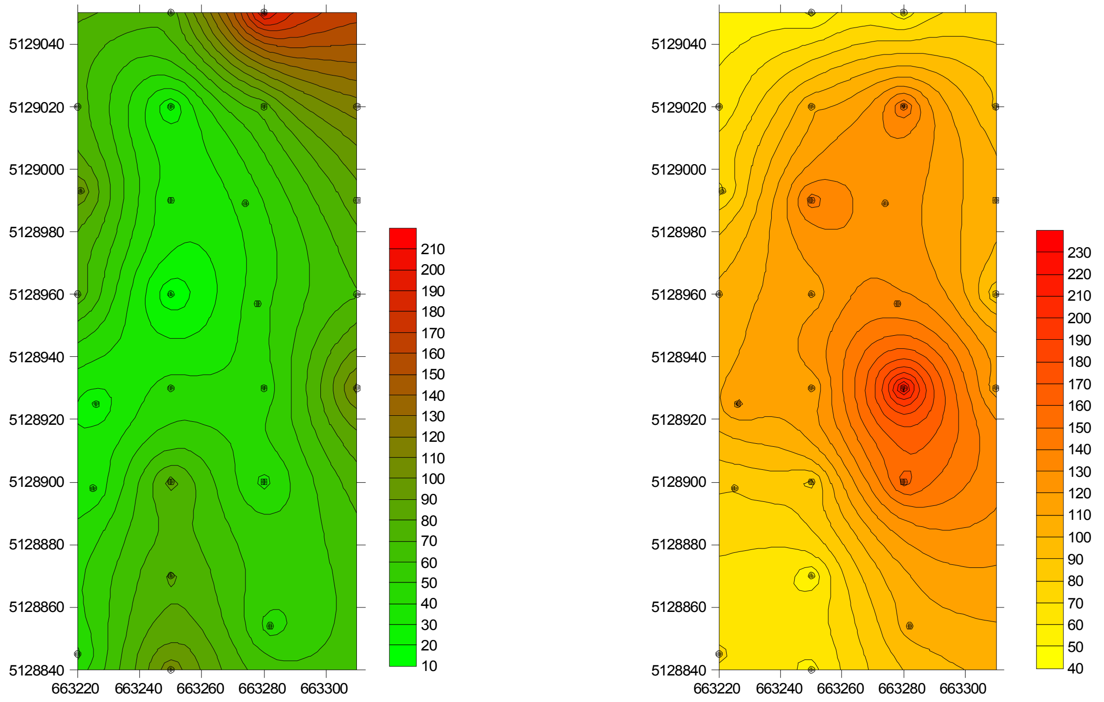


Fig. 4.16: spatial distribution of AMD parameters (pH and NAPP) at the Hop waste-rock dump. UTM coordinates and parameter range of variation are reported.


Ag spatial distribution

Cu spatial distribution


Zn spatial distribution

As spatial distribution

Fig. 4.17: spatial distribution of selected PTE at the Hop waste-rock dump. UTM coordinates and parameter range of variation are reported.

Contour maps well represent the spatial heterogeneity of the geochemical features of the Hop waste rock-dump and the relationship between pH values and AMD production potential. In particular, the central part of the dump is made mainly by WR1 samples and is characterised by the highest NAPP values, which correspond to acid condition (pH values from 3.0 to 4.5) and highest As concentrations, ranging from 120 to 230 mg/kg. On the other hand, the edges of the dump are made mainly by WR2 samples, showing negative NAPP values, corresponding to pH values ranging from 6.0 to 8.4 and Cu and Zn highest contents (56 and 210 mg/kg, respectively). However, these two metals do not reach hazardous concentrations. The spatial distribution of these important environmental variables suggests that the current way to stock such different waste-rock materials could be improved, in order to minimise negative impact on environment.

4.2.9 Conclusions

The East Hop dump consists of heterogeneous material composed by two different rock types: (1) the so-called WR1 samples, mainly characterized by dacite fragments; and (2) the WR2 samples that mainly consist of andesitic breccias.

At present, the waste rock dump is a source of acid drainage. Fifteen of twenty-five samples have positive NAPP (an average value of 34 kg H_2SO_4/t), although the sulphur concentrations found are not so high compared with other mining sites (Nordstrom et al., 2000; Morin & Hutt, 2001). In terms of AMD features:

- the WR2 group has ANC > MPA, and it is therefore able to buffer the production of acidic water;
- the WR1 group has always nil ANC and positive MPA; therefore, it is a source of acid drainage.

In general, the concentrations of PTE into the waste rocks are below the regulatory limits (Carlon, 2007), with the exception of As, which has concentrations up to 10 times higher than those prescribed by law.

These results are confirmed by kinetic tests, as:

- leached waters that interacted with WR2 samples are characterised by pH mean value equal to 8.2;
- leached waters that interacted with WR1 samples are acid (pH mean value 3.7) and could bring to a higher PTE geochemical mobility.

This study outlines that a more accurate management of waste materials could have prevented AMD processes associated with it and the subsequent leaching of heavy metals. The evidences coming from both field observations and preliminary analyses on surface waters (RMGC, 2006) indicate that the mine dump contributes to some extent to environmental pollution, while it is conceivable that most of the processes take place in the underground tunnels of the mine. This is confirmed by the physico-chemical characteristics of the drainage waters: whereas waters draining galleries are characterised by pH lower than 3, the waters draining Hop dump have pH around 6 (Azzali, 2011). The lowest pH values can be due to the presence of sulphide veins hosting Au mineralization, where the average content of sulphur in the parental rock is higher than that in the dump that represents the mine wastes. Moreover, the circulation of water can leach preferentially underground mineralization in the veins also for longer contact time. For this reason it will be also necessary to conduct future surveys for more detailed modelling of groundwater flow and migration of PTE in the environment.

The results of the leaching tests conducted by Costin et al. (2011) are in agreement with the results of static and kinetic tests conducted in the present work, i.e. giving rise to acidic water in the case of drainage of mainly dacitic materials and neutral water in the case of drainage of predominantly andesitic materials. However, the tests of Costin et al. (2011) did not take into account the buffering power of the andesitic WR2 and the spatial distribution of the different lithologies. The overall result of the water—waste material interaction is that drainage waters are only slightly acidic.

The best way towards obtaining the full picture of the AMD processes in the area is to execute a campaign of systematic WR sampling and to run static tests on all the samples and kinetic tests on a selection of samples. The results of both the tests, applied to a correct hydrological model of the site will be useful to understand the dynamics of pollution phenomena.

4.3 Hop waste-rock dump vegetation

4.3.1 Plant species description

Hop waste-rock dump is colonized by few individuals of pioneer native tree species, as *Salix* spp., *Betula pendula* (*B. pendula*) and *Populus tremula* (*P. tremula*) which grow on the central area and on its slope, as shown in figures 4.18. *Pinus sylvestris* (*P. sylvestris*) is also present, but it grows only on the dump edge, near the wood surrounding the area.

Fig. 4.18 a and b: native vegetation growing on Hop waste-rock dump and on its slopes.

As reported in the pertinent literature, tree species are generally not able to adapt to high concentrations of heavy metal in soil, resulting in the evolution of only a few metal-tolerant ecotypes, as *Salix* and *Populus* species, whose metal tolerance is widely known and described in literature. The genetically highly variable Salicaceae family, with its genera *Salix* (willows) and *Populus* (poplars), comprises a large number of woody species and hybrids, many of which became adapted to ecological niches such as nutrient-poor, dry or wet and metal-contaminated environments (Dickinson and references therein, 2000). Accordingly, this family represents a rich resource for identification of species with high metal resistance and high or low metal uptake, as it has been addressed in recent studies, regarding the metal resistance and accumulation potential of various willow and poplar species in field surveys (Stoltz and Greger, 2002; Chang et al., 2005; Unterbrunner et al., 2007) and hydroponic experiments (Noel Dos Santos Utmazian et al., 2006; Mleczek et al., 2009). Other tree species are known for their capability to grow on metal-contaminated sites: *B. pendula* is a common species growing on disturbed area and mining spoils, showing tolerance to Zn and Al (Kopponen et al., 2001); its usefulness as Pb and Zn bio-indicator has also been tested (Marguì at al., 2007). Moreover, *P. sylvestris* grows on Zn and Cu contaminated mine waste (Adriaensen et al., 2006).

4.3.2 Plant chemical analyses

In order to evaluate the potential PTE contamination of the vegetation growing on Hop waste-rock dump, eleven plant specimen belonging to four different species were collected in the same earth material sampling place. In particular, five specimen belonging to *Salix* spp. (aboveground tissues), two to *P. tremula* (both aboveground and root tissues), two to *B. pendula* (aboveground tissues) and to *P. sylvestris* (needle-leaf tissues) were collected. Sampling was made in the early autumn, between late August and early September, when metal accumulation in leaves is supposed to be highest (Pulford and Watson and references therein, 2000). Bio-geochemical analyses are reported in Appendix A.5.

In Table 4.5 selected geochemical features of the waste rocks colonized by wild flora are summarized and data are expressed as range of variation. Acid pH values and As contamination (range 70-230 mg kg^{-1}) occurring on Hop waste-rock dump are stressful conditions for plants, but these species are able to tolerate such constrictive situations, with the exception of *P. silvestrys,* that grown on different kind of substrate on the edge of the dump.

Plant species	**pH**	**EC** µS/cm	**Cu**	**Zn** mg/kg	**As**
Salix spp.	3.0 – 7.7	111 – 1,890	12 - 55	10 - 85	73 - 166
B. pendula	4.5 – 7.5	250 - 920	21 -32	32 - 43	148 - 231
P. tremula	4.7 – 5.0	110 - 250	18 - 21	10 - 43	112 - 231
P. sylvestris	7.3 – 7.4	1,350 – 1,960	38 - 41	91 - 97	58 - 77

Table 4.5: geochemical features of waste rocks colonized by native species, data are expressed as range of variations.

In particular, *Salix* spp. represents the species more able to adapt to these limiting conditions, as known from the literature and confirmed from this study. On the Hop waste-rock dump these trees behave as a pioneer species, which grown on substrates characterized by very different pH values (range 3.0 – 7.7).

According to the biogeochemical analyses summarized in Table 4.6 and shown in figures 4.18 and 4.19, Zn is stored mainly in leaf tissues (see also figure 4.18), where it reaches the greatest values, ranging from 300 to

630 mg/kg. On the other hand, Cu content are higher in branches (range 17 - 63 mg/kg) than in leaves (range 21/44 mg kg). Arsenic shows the same behavior of Zn, as As levels are higher in leaf tissues, where it reaches the maximum values of 45 mg/kg.

B. pendula and *P. tremula* grow on strong As contaminated substrates, with the highest concentrations of 230 mg/kg. All elements are stored mainly in leaves, as shown in figures 4.18 and 4.19. Moreover, *B. pendula* was found to have the greatest Cu and Zn tolerance capability, showing the highest leaf content (with maximum values of 1,025 mg/kg for Zn and 90 mg/kg for Cu).

	Cu	**Zn**	**As**
Plant species and tissue		mg/kg	
Salix spp.			
Leaves (n = 5)	27 (21 - 45)	351 (302 - 632)	26 (25 - 45)
Roots (n = 2)	40	299	23
B. pendula			
Leaves (n = 2)	79	634	38
Branches (n = 2)	61	194	22
P. tremula			
Leaves (n = 2)	75	426	27
Branches (n = 2)	63	126	26
Roots (n = 2)	29	40	31
P. sylvestris			
Leaves (n = 2)	11	35	2
Normal ranges in plants	5 - 30	27 - 150	1.0 – 1.7

Table 4.6: selected PTE content in plant tissues. Data are expressed as mean values and range of variation (data inside parenthesis), while n represents the number of specimen collected and analysed.

On the other hand, *P. sylvestris* grows on earth materials characterized by lower As contents (58-77 mg/kg) and circum-neutral pH values (ranging from 7.3 to 7.4), on the edge of the dump, and therefore does not seem to tolerate strong acid conditions that characterize a wide surface of the Hop waste-rock dump. PTE contents in its tissues are lower when compared with other species, not only for Zn but also for Cu and As.

Considering the low numbers of samples, these preliminary results should be confirmed by further study.

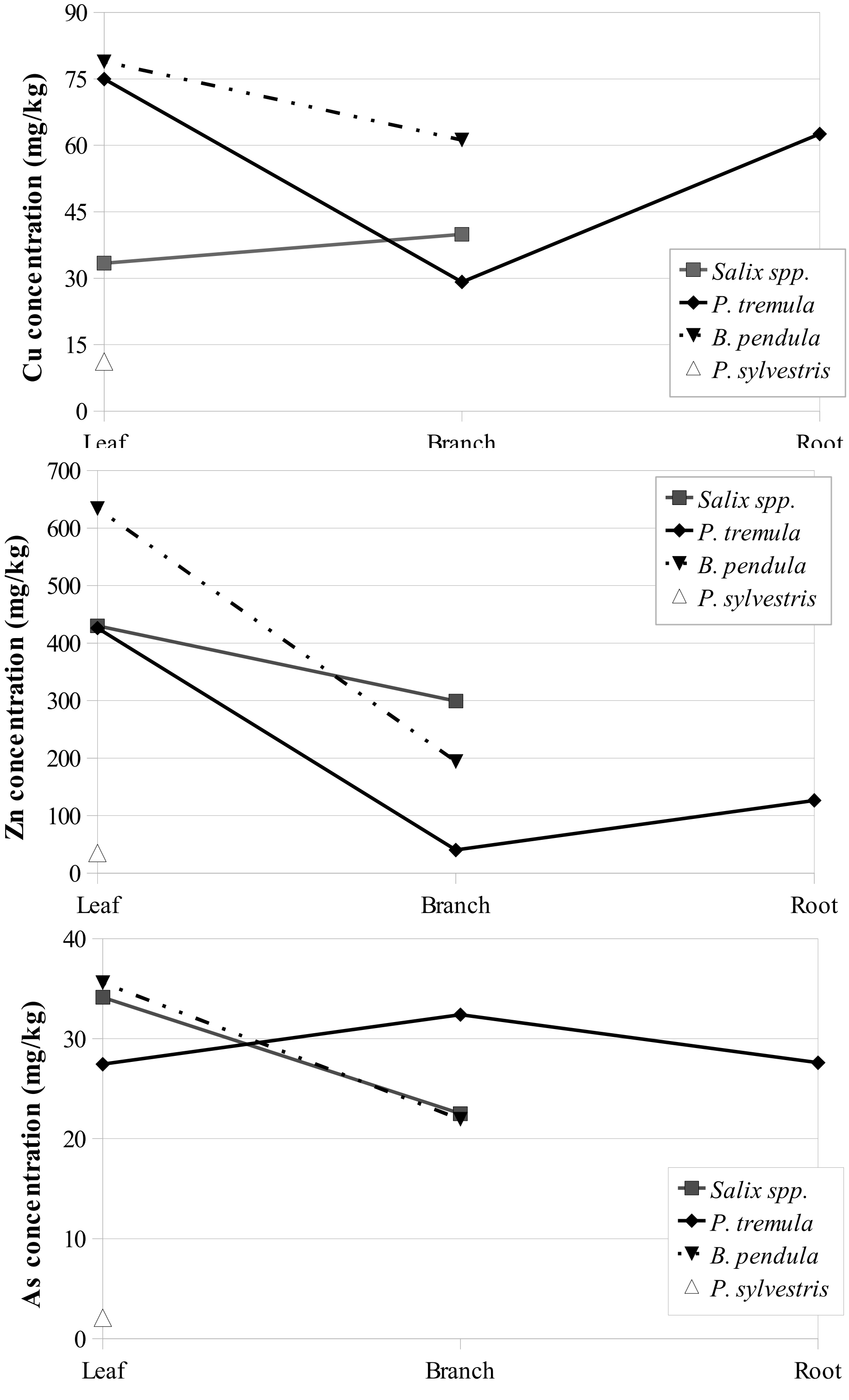


Fig. 4.18: Cu, Zn and As contents in plant tissues.

4.3.3 Identification of metal tolerance strategies

For all species BF and TF were calculated in order to identify the different metal tolerance strategies of each species, as shown in Appendix A.5.

In *Salix* spp., *B. pendula* and *P. tremula* BF values are > 1 for Cu (range 1.2 – 4.5), >>1 for Zn (range 1.2 – 56.5) and < 1 for As (range 0.1 – 0.6) in all tissues. Cu and Zn were found especially in leaf tissues, with a maximum bioaccumulation capacity found in *P. tremula*, which shows a maximum BF value of 56.5 for Zn and 4.5 for Cu. In leaves BF values for Zn are one order of magnitude higher than those for Cu, according to the different biological role of these two metals.

On the other hand, As concentration in leaf tissues is significantly lower than in soils, exceeding however the toxic values reported in the pertinent literature (see Appendix 7). This element is generally accumulated in leaves (or in roots in the case of *P. tremula*) and its concentrations are one order of magnitude lower than those of Zn. *P. sylvestris* shows a different behavior: its BF values are << 1 for Cu (mean value 0.3) and Zn (mean value 0.4) and close to 0 for As. This plant species employs a strong exclusion-strategy, immobilizing PTE in soils and reducing their bioavailability, so maintaining low levels in its tissues.

Results are consistent with the biological role of Zn, which is an essential micronutrient that can be well tolerated within a limited range of concentrations, while As does not have any physiological role and is highly toxic even at very low levels. These data suggest therefore that an exclusion metal-tolerance strategy may work in synergy with physiological detoxification mechanisms, as As tissue contents in all species are higher than normal ranges in plants.

4.3.4 Conclusions

Hop waste-rock dump is a highly variable substrate, characterized by stressful conditions for plant growth such as acid pH values and As contamination (mean value 80 mg kg^{-1}), while Cu and Zn contents respectively reach 50 and 90 mg kg^{-1}.

Preliminary data confirm that *Salix* spp., *B. pendula* and *P. tremula* are able to tolerate such limiting conditions, as known from the literature. They actively accumulate Cu and Zn in their tissues, specially in leaves, with BF values significantly high for Zn (range 1.2 – 56), although they can not be considered as hyper-accumulators. On the other hand, the same species act as excluders for As, whose concentration in plant tissues are lower than in soils, exceeding however toxic values.

Conversely, *P. sylvestris* acts as a strong excluders, avoiding PTE accumulation in its biomass, where As contents are a little bit higher than normal ranges found in most species. These data suggest that an exclusion metal-tolerance strategy may work in synergy with physiological detoxification mechanisms.

Salix spp. represents the species more able to tolerate different environmental situations and to grow on strong acid substrates, acting as a pioneer species that could be used for revegetation of mine lands and stabilization of dump slopes, even on the area still not vegetated. However, these species accumulate eco-toxic elements in their leaves, such as Cu and Zn, that are actually moving from substrates to living beings, with a potential geochemical hazard.

Chapter 5

Application 2: Gromo and Gandellino mining area (Valseriana, Northern Italy)

Near Gromo village, on both sides of the Valseriana in the Central Orobic Alps (Bergamo, Italy), several proofs of historical mining activities are present. Since 21th century these mines, exploited specifically for Fe and Ag, historically played an important rule for the economic development of the valley. The mine area is not exploited at the present time, but the numerous underground cavities testify the historical activities linked to the exploitation of Fe, Zn, Pb, Ag, Cu mineralisations.

Previous studies showed that no AMD processes are on-going in the area; however this ancient mine site is characterised by the presence of several waste-rock dumps, some of them located very close to villages, that could represent a source of PTE contamination in the neighbouring environment. For this reason, two ancient mine sites have been were studied in detail in this work.

The first is the waste-rock dump located very closed to Ripa village, called Coren del Cucì. It is a 40,000 m^2 wide mining waste made by stone scraps. Here a wide vegetation made only by *Calluna vulgaris* grows, while the same species has not been founded in neighbouring areas.

Moreover, other mining waste areas have been investigated; they are smaller than the first one and are located near the localities of Gromo and Gandellino. In this case the boundaries of the waste area were not clearly identifiable, due to the abundant presence of wild vegetation; in particular the pioneer species *Dryopteris filix-mas* that grows above these sites was investigated.

5.1 Site overview

5.1.1 Site description and ore-mineral chemistry

Several evidences of mining activities occurred between Gromo and Gandellino villages, on both sides of Seriana Valley. The oldest mines are called “Coren del Cucì”, name coming from the old cliff that dominates the medieval village of Gromo. The mine is composed by a complex of galleries and voids, developing underneath the historical centre of the village. Since the 11th century, these mines had been exploited for Ag, Cu, Fe, Pb and Zn (Jervis, 1881) and played an important role for the economic development of the valley. Gromo was a centre of international mining trade and it was named “little Toledo”, due to the high value of the sword that were produced. The ore deposits, made up mainly by sulphides, sulphosalts and carbonates, were hugely exploited in the Middle Ages and abandoned in the early decades of the 20th century, after a disastrous flood that destroyed Gromo village and its neighbours. Working mine did not ever resume, due to the scarce current value of deposit stock and its limited availability.

From the geological point of view, the studied area is located in the Central Orobic Alps (see Figure 5.1), where four main litho-stratigraphic units crop out:

- Crystalline Basement [Pre-Carboniferous];
- Base Gravel [Late Carboniferous-Early Permian];
- Sulphide Quartz Breccia [SQB – Permian?];
- Collio Formation [Early-Middle Permian].

The relations between these litho-stratigraphic units are very complex due to the occurrence of multiple tectonic structures located near the area. Here outstanding SQB bodies crop out along the contact between the crystalline basement and the volcano-sedimentary cover rocks. Several isolated SQB bodies occur mainly in Ripa, Pradel, Gromo, Vedriol and Gandellino localities, thereby defining a small area of 9 km^2 outcropping along WSW-ENE faults between the villages of Gromo and Gandellino. Detailed studies of the SQB bodies in the Gromo-Gandellino area proved that their development may be in relationship to fault-related hydrothermal activity (Servida et al., 2010). The breccia bodies can be therefore clearly distinguished by other non-hydrothermal fragmental rocks outcropping nearby. Presently, the SQB outcrops carry only small, mm- to cm-sized sulphide nodules; however the mining voids (up to 1 m wide and up to 10 m long) left on several SQB outcrops and the presence of the mine dumps suggest that the ore deposits may have been rather rich.

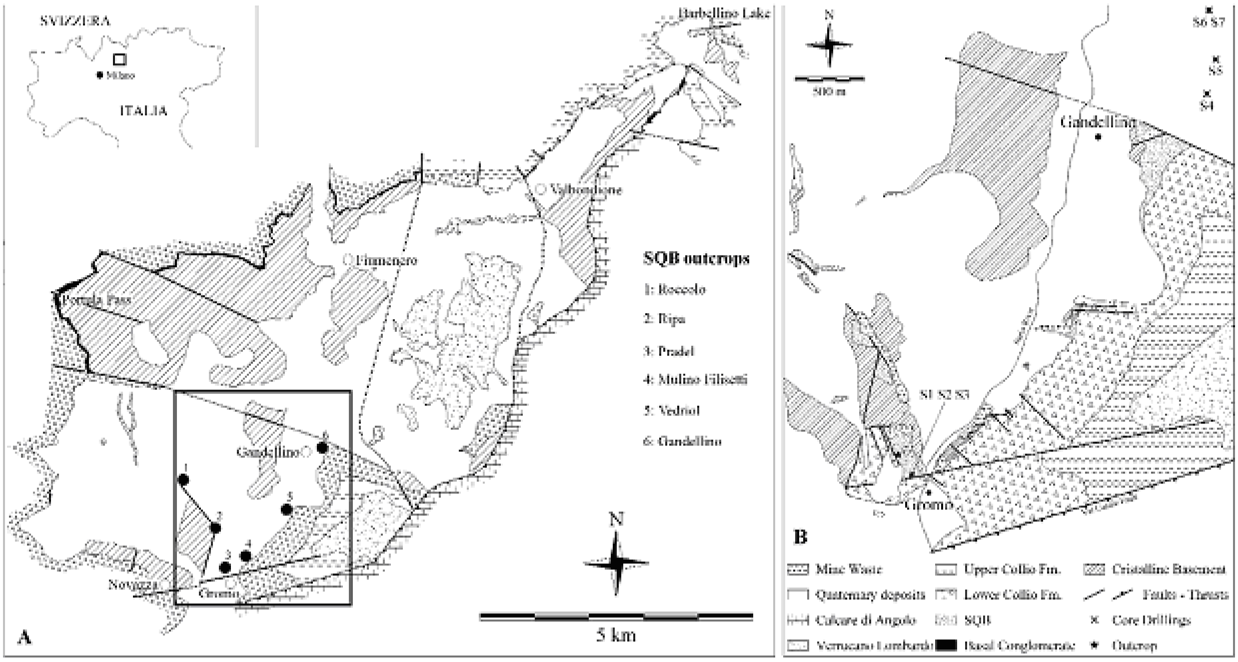


Fig. 5.1: A - localisation of the Gromo-Gandellino ore-bearing SQB outcrops and waste-rock dumps; B - geological sketch map of the Northern Valseriana (Servida et al., 2011).

The ore mineralization is represented by a polyphasic association of sulphides and sulphosalts containing Ag, As, Co, Cu, Fe, Ni, Pb, Sb and Zn; dominant chalcopyrite and tetrahedrite are accompanied by variable amounts of galena, sphalerite (locally dominant), minor Co-Ni-Fe sulpharsenides (gersdorffite-cobaltite and arsenopyrite) and pyrite, accessory pyrrhotite, marcasite, mackinawite and rare native silver (Moroni et al., 2003; Servida et al., 2010). Ore minerals, as well as siderite and quartz, occur in different generations, as indicated by the textural relationships and the compositional variations of some of the ore minerals. The ore features suggest a mineralising process characterised by deposition, replacement, cataclasis and minor recrystallization in hydrothermal conditions. The latter can be better explained by the chemical characteristics of some of the ore minerals (Servida et al., 2010).

The presence of pyrite and other sulphides could trigger off AMD phenomena, which often takes place in sulphide-bearing areas and could lead metal remobilisation toward rivers and ground waters. Preliminary tests, made on earth materials in order to highlight the acidity making potential, showed the absence of acid mine drainage processes, probably due to the abundant occurrence of siderite among the main ore phases. Moreover, chemical analysis of groundwater that springs off near Coren del Cucì dump agree with this evidence, as confirmed by their pH values about 7 (Moroni et al., 2003)

5.1.2 Waste-rock dumps

Dumps are located in an area spreading to the north of Gromo village, both on the right and the left side of Serio River (Figure 5.1 A). The main dump, called Coren del Cucì, develops between 700 and 1040 m a.s.l. on a surface of 10,500 m^2. It is highlighted by the colour of the covering shrub vegetation, mainly made by *Calluna vulgaris* (*C.* vulgaris, shown in Fig. 5.2), that does not grow on the surrounding area, as shown in Fig. 5.4.

The other small waste disposals are located close to the access of galleries. Pradel dump is made by scarce materials (only some ten m^2) located on the right side of Serio River: it is characterized by poor vegetation, mainly made by *Dryopteris filix-mas* (*D. filix-mas*, shown in Fig. 5.3), that prefers shady places and grows exclusively close to the access of galleries, while on the dump materials outcrop vegetation is lacking. Vedriol dumps outcrop on the left side of Serio river between 600 m a.s.l. and 1200 m a.s.l. on a surface of 1,000 m^2. They are characterized by an abundant presence of woody plants that partially grow near their edges, so they are not clearly identifiable. They are covered also by *D. filix-mas*, often present outside the mine dumps too (see Fig. 5.6).

5.1.3 Plant species description

Two tolerant species are growing: *C. vulgaris*, which is the only one that grows on the Coren del Cucì dump, and *D. filix-mas* which grows mainly close to the access of galleries and also on Pradel and Vedriol dumps.

Fig. 5.2 *Calluna vulgaris.*

Fig. 5.3 *Dryopteris filix-mas.*

C. vulgaris is a widespread and common species that usually grows in sunny places on acid and nutrients-poor soils (Gimingham, 1960; 1972) Like other species of Ericacea family (Abreu et al., 2008), it is characterized by a constitutive metal tolerance, even if ecotypic differentiation of populations growing on polluted and not-polluted areas has also been suggested (Burt, 1984). In Great Britain and Germany was observed that *C. vulgaris* is very tolerant to heavy metals occurring on different substrates, e.g. serpentine and polluted soils (Marrs & Bannister, 1978; Eltrop et al., 1991; Pratas et al., 2005). This plant species uses to form an ericoid mychorrizal association (ERM) with the fungal *Hymenoscyphus ericae* that plays an important role in metal tolerance by preventing metal translocation to the growing parts of the plant, allowing the accumulation of high concentrations of Cu (Burt, 1984; Bradley et al., 1982; Monni et al., 2000) and reducing the arsenate assimilation (Silver & Phung, 1996; Rosen, 1999; Sharples et al., 2000). Mychorrizal associations are also known to provide their host with organic nitrogen (Bending & Read, 1997; van der Wal et al., 2009), which is commonly lacking in waste-rock dumps.

On the other hand, many fern species are important bioindicators of metal-bearing soils (Kachenko et al., 2007). Some ferns of the Pteridaceae family, including *Pityrogramma calomelanos* L. (Francesconi et al., 2002; Visoottiviseth et al., 2002) and many species in the *Pteris genus* (Meharg & Hartley-Whitaker, 2002; Zao et al., 2002) show As accumulation capacity. Some plants of *D. filix-mas* collected from serpentine soils in the Ligurian region (Italy) was able to mobilise metals, even below the limits of Cd hyperaccumulation (Cornara et al., 2007). The same species was also found as pioneer colonizer of As-rich mine waste in Cornwall, UK (Wilkins & Salter, 2003).

5.1.4 Sampling

Due to its dimension and its proximity to Gromo village, Coren del Cucì dump was chosen for the principal investigation. The earth material (natural soil and waste rocks) sampling was performed according different transects, as shown in Fig. 5.5: three transects cross the landfill and extend along the slope on both sides, while five transects cover only the area inside the dump. Each transect was designed at a distance of about 100 meters from the previous. A total of 54 earth material samples of were collected: for each transect two/four inside samples were spaced about 10 m from each other and eight outside samples were spaced 25 m from each others. One sample was taken about 700 m far from the main dump (sample called GRO-08), where both the studied plant species were found. This sample is represented in Fig. 5.6 by a red point; the other points show the localisation of the samples collected at Pradel and Vedriol mine areas. An amount of 11 samples were gathered with a random distribution at Pradel waste dump. On Vedriol dumps 10 samples were collected, where a half of the samples were collected where the occurrence of waste materials was evident, the other half at a distance between 10 and 50 m far from them.

Fig. 5.4: Coren del Cucì waste-rock dump, located very close to Ripa locality; in foreground , Gromo village.

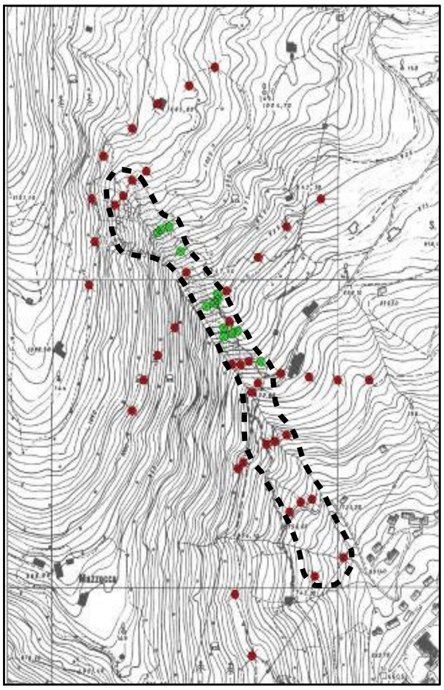


Fig. 5.5: Coren del Cucì sampling area. The waste-rock area is surrounding by a black dotted line. Green dots are vegetation samples, while red dots are earth material samples

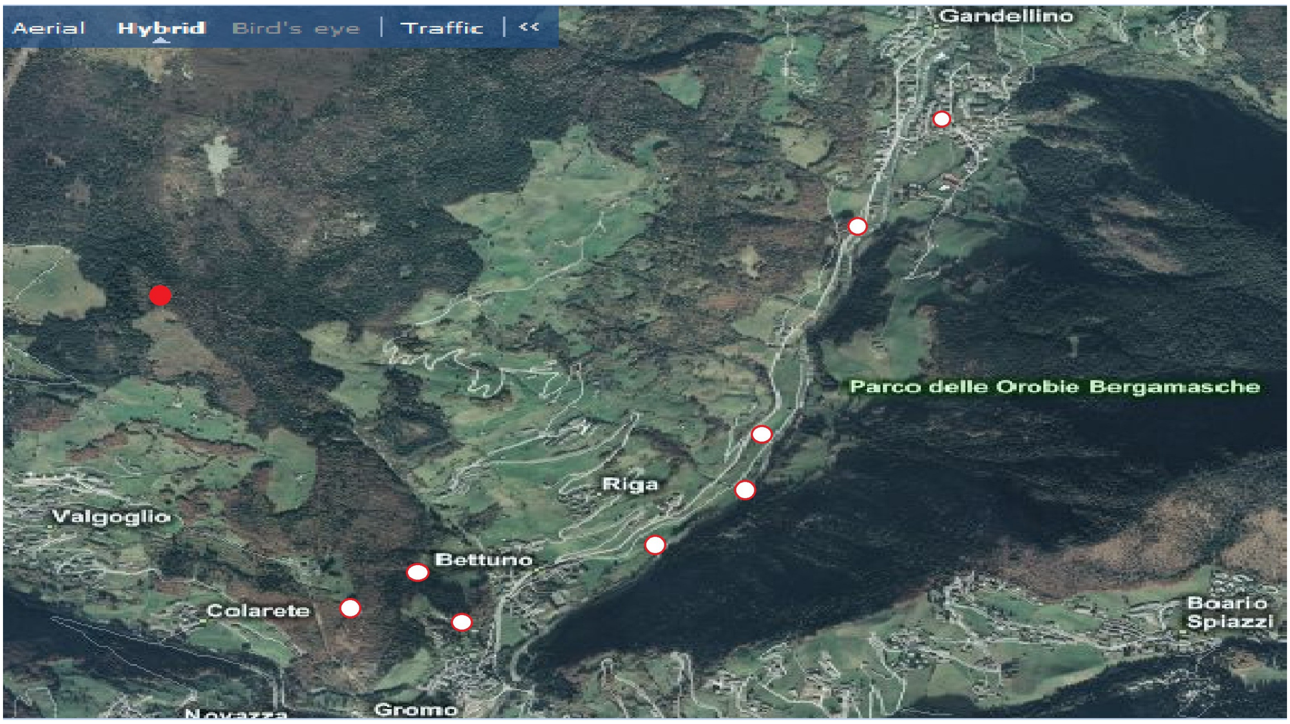


Fig. 5.6: Gromo-Gandellino mine area and sampling places, represented with white points. The red point represents the samples called GRO-08.

A significant amount of plant tissue both above and underground was collected in the same substrate sampling places. In total 12 aboveground and 3 underground tissue samples of *C. vulgaris* were collected at Coren del Cucì, while 16 aboveground and 6 underground tissue samples of *D. filix-mas* were collected at Pradel and Vedriol. A sample of both species was also collected 700 m far from the mineralized area (GRO-08).

All the collected samples were analysed by relative guideline procedures and statistical elaboration. Results are shown in Appendix B.

5.2 Earth materials characterisation

PTE and pH of earth material are shown in Appendix B.1, as concentration ranges, means and standard deviations.

The three dumps show different element associations (see Table 5.1 and Figure 5.7): As, Cu, Pb and Zn prevail in Coren del Cucì site; Pb and Zn in Pradel dump and Vedriol site is characterised by As, Co, Cu, Ni and as main elements. As a matter of fact the different metallic paragenesis agrees completely with the occurrence of sulphides and sulphosalts which were previously detected by means of optical and SEM analyses (Servida et al., 2010).

	Element mean concentration and relative percentage											
Sampling area	**Zn**		**Cu**		**Pb**		**Co**		**Ni**		**As**	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Coren del Cucì	1,019	28	957	26	573	16	175	5	85	2	864	23
Pradel	3,540	49	295	4	3,194	44	38	-	51	-	199	3
Vedriol	12	-	311	29	17	-	218	20	105	10	445	4

Table 5.1: different trace element association in the three studied sites, data are expressed as mean concentration (mg/kg) and relative percentage.

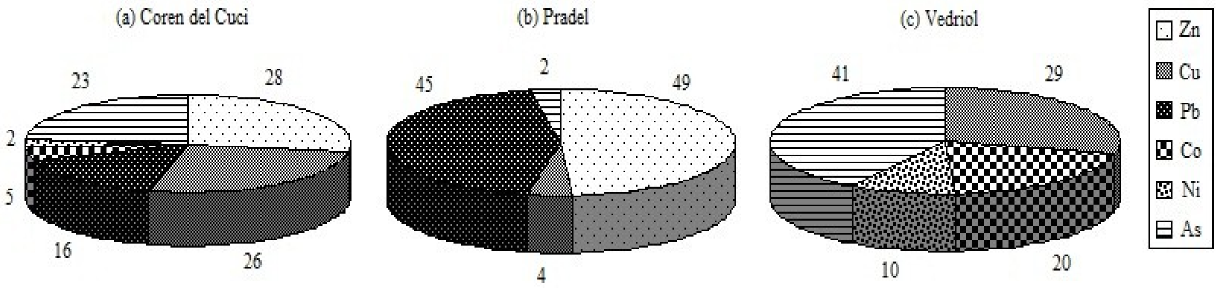


Fig. 5.7: element associations at the three mine site (Coren del Cucì, Pradel and Vedriol).

As shown in Appendix B.1, in earth materials all the PTE reach high concentrations. If only mean values are considered, Zn and Pb respectively exceed 3,500 and 3,000 mg/kg at Pradel, while Co and Ni exceed 200 and 100 mg/kg at Vedriol dumps. Ag and Cd mean concentrations is lower than other elements, reaching 25 e 20 mg/kg. Arsenic reaches very high concentration in all areas, with a maximum mean content of 868 mg/kg at Coren del Cucì dump, located very close to Gromo village.

High contents of metals and As were found also in soils far from Coren del Cucì waste rock accumulation, so confirming that the Gromo-Gandellino area is characterised by a natural anomalous concentration of PTE, related to the mineralization, which greatly raise at dumps. For this reason the area should be controlled in order to ensure a healthy environment.

High standard deviation values indicate an irregular distribution of the residual ore minerals into dumps, mainly owing to the presence of richer samples close to the access of galleries. High standard deviations are also observed in the external samples of Coren del Cucì, due to the different distance from the waste materials. Figure 5.8 shows the variation of As concentration along the transect that intersects Coren del Cucì dump in the middle part (900 m a.s.l.) and extends for about 100 meters to his right and his left.

The pH value of earth materials is a very important geochemical variable, as it affects metal mobility in soil (Conesa et al., 2005) and the answer of plants to metal toxicity (Wong, 2003). All the samples show slightly acidic pH values, ranging from 4.0 to 6.0. The lowest one was found at Vedriol dumps (mean value = 4.58). The pH values are generally lower than 6.5, value commonly recognized as the optimum for nutrient availability and corresponding to a low availability of most PTE, with the exception of As that becomes more mobile (Kabata-Pendias, 2011). Slightly acidic pH values found at Coren del Cucì agree with the ecology of *C. vulgaris* that grows on litter rich in phenolic compounds, which decompose slowly and modify soil conditions causing acidification and organic matter accumulation (Gimingham, 1960; 1972).

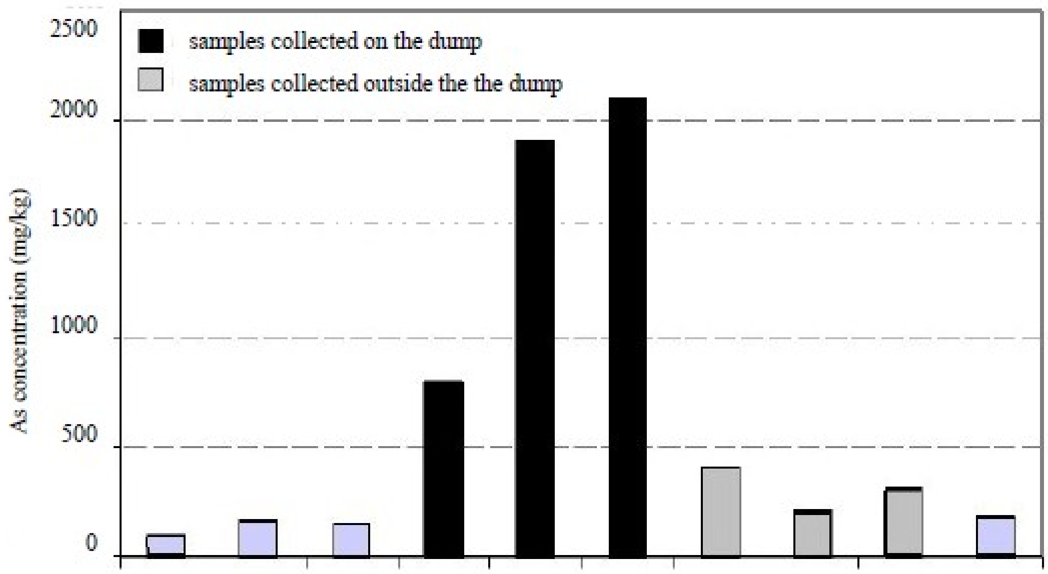


Fig. 5.8: different As content along the cross-line at Coren del Cucì (900 m a.s.l.).

5.3 Vegetation

5.3.1 Plant chemical analyses

PTE concentrations in both plant species, regarding to aerial parts and roots, and BF and TF values are shown in Appendix B.2. The box-plots represented in Figure 5.8 and 5.9 show the different PTE content in the plant tissues for both species.

C. vulgaris in the Gromo-Gandellino area seems to grow exclusively on Coren del Cucì waste dump. The aerial parts show high contents of all PTE exceeding the baseline values indicated for leaf tissues (Kabata-Pendias, 2011), with the exception of Zn and Cu. PTE mean contents in the roots are always one order of magnitude higher than leaf ones and they overcome the limits of toxicity for all elements. Cu and As concentrations are particularly high (858 and 149 mg/kg respectively). On the other hand, Cd and Ag show low concentrations, close to the detection limits. The only sample collected far from the mineralised area (GRO-08) shows a different behaviour: all the examined PTE, with the exception of Pb, are below the level of normal concentrations both for aerial parts and roots.

C. *vulgaris* shows several BF values >1, displaying an evident tendency to accumulate metals. This behaviour is especially evident in the root tissues, where BF values are 1.09 for Co and 2.37 for Zn. BF values >1 are also characteristic of aerial part for Zn (1.26), Ni (1.01) and Cd (2.90), the last one showing the highest value. On the other hand, despite As concentration at Coren del Cucì dump is very high, BF values are very low and close to zero in leaves. These results confirm that *C. vulgaris* is able to grow on As contaminated substrates by employing an exclusion-strategy. TF values are below 1, with the exception of Cd, that range from 0.14 to 1.32. These data are consistent with the previous observations on the behaviour of *C. vulgaris* as metal bio-accumulator, when it occur around mine sites (Monni et al., 2000; Wilson & Pyatt, 2007).

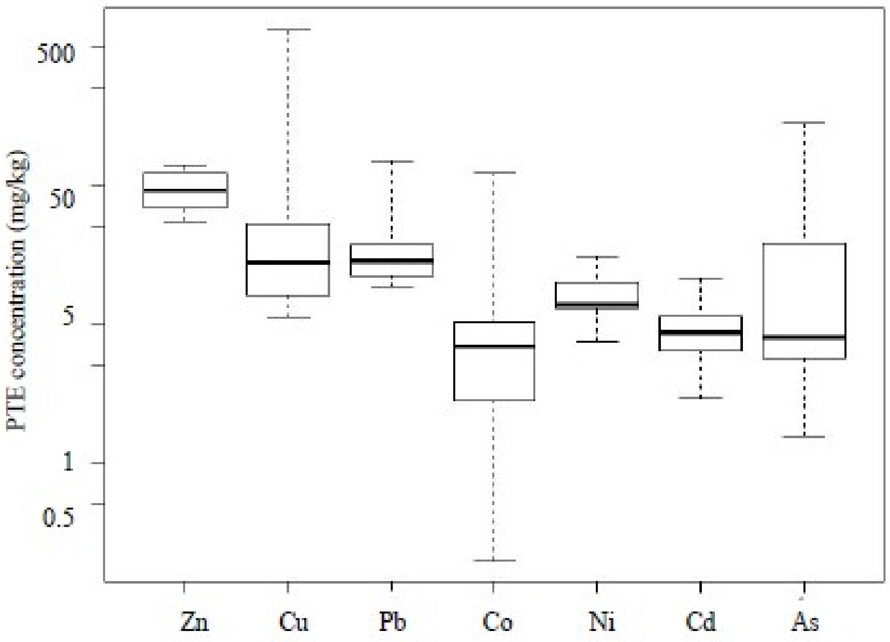


Fig. 5.8: box-plot showing different PTE contents in plant tissues for *Calluna vulgaris*.

Leaf concentration levels in *D. filix-mas* are similar to those related to the baseline (Kabata-Pendias, 2011) or slightly exceed this limit, reaching toxic content only for As and Pb at Vedriol site. PTE concentrations in the roots are higher than in leaves and As reaches value of 100 mg/kg. The plant collected far from the mineralised area shows baseline Zn and Cu concentrations, while other element contents are close to the lower analytical limits. These results are in agreement with the physiological role of Zn and Cu that are essential elements for plant growth.

On the whole, BF values are low and below 1 for all the PTE, except for Ni for roots in Pradel and Zn, wich shows values >1 for aerial part and roots in both mine areas. All TF values are below 1, except for the samples growing on the sites far from Vedriol dumps, which accumulate more Zn in aerial part than in roots, so confirming the biological behaviour of this element.

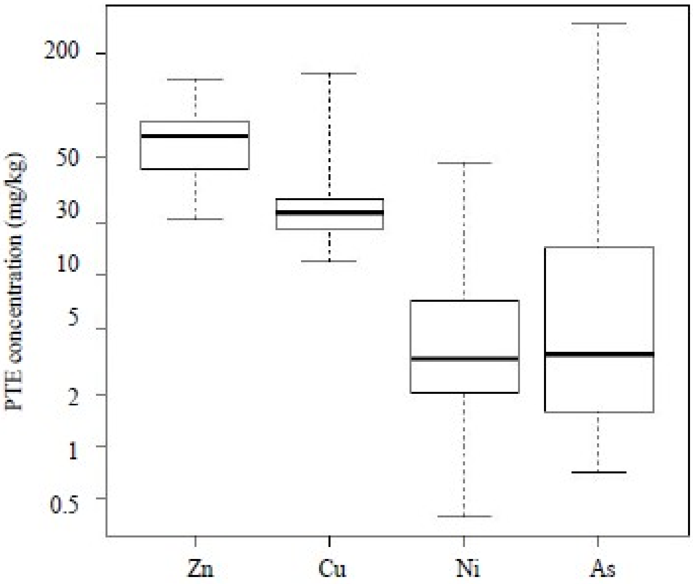


Fig. 5.9: box plot showing different PTE contents in plant tissues for *Dryopteris filix-mas*.

A better comparison between aerial part and roots was performed comparing average values made both on root and aerial part of plants collected on the same earth material sample. In *C. vulgaris* and *D. filix-ma*s species, three and five samples can be compared, respectively. In the *D. filix-mas* species Co and Cd were excluded from the comparison due to low concentrations (lower than the detection analytical limits). Average concentrations were plotted in figures 5.10 and 5.11. The two species show similar behaviour with regard to the elements examined, showing the roots blocking Pb, As and Co, in addition to Cu, which assumes particularly high concentrations in the roots of *C. vulgaris*.

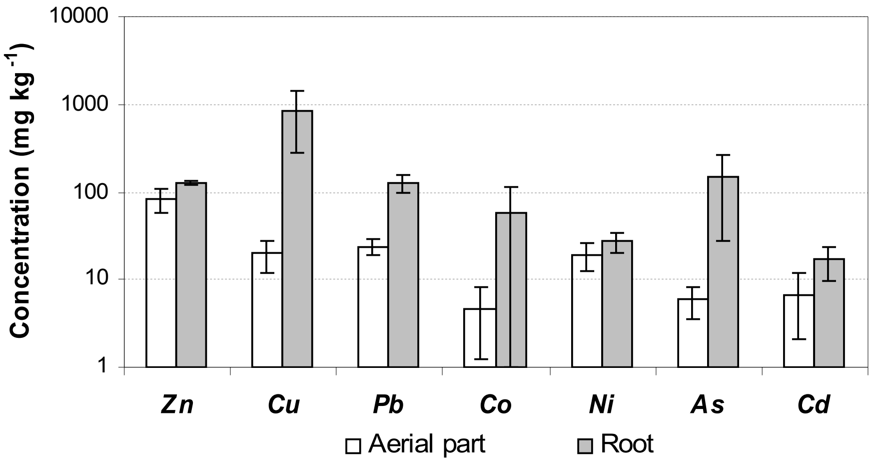


Fig. 5.10: Aerial parts and roots comparison for *Calluna vulgaris* samples at the same location (three samples). Concentrations were plotted on a logarithmic scale.

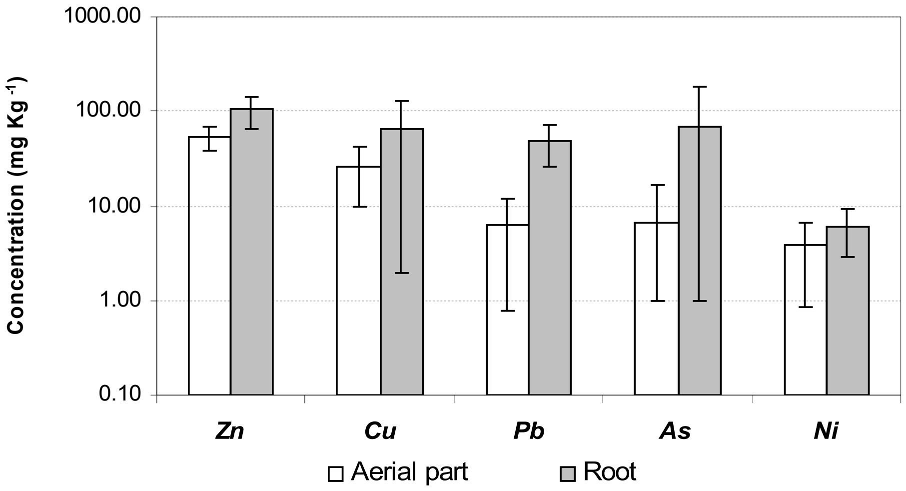


Fig. 5.11: Aerial parts and roots comparison for *Dryopteris filix-mas* samples at the same locality (five samples). Concentrations were plotted on a logarithmic scale.

5.3.2 Identification of metal tolerance strategies

Concentrations in *C. vulgaris* and *D. filix-mas* aerial parts are far below those that characterise hyperaccumulator species (Baker, 1989). Moreover, they show a scarce mobilization of metals from soil to aerial parts, thus acting as excluders (Baker, 1981).

C. *vulgaris* has the lowest enrichment coefficient, even if it grows on soils characterized by the highest heavy metal concentrations. It can also tolerate very high As content, by preventing its accumulation in leaves. These results confirm its strong tolerance to toxic elements, so it can be considered as a pioneer plant useful for the restoration of vegetation cover in mining areas.

5.4 Conclusions

Data elaboration led to confirm the presence of an environmental hazard for the area that is amplified by the waste-rock dumps, where soil heavy metal concentrations is about one order of magnitude higher than in natural soils (Kabata-Pendias, 2011). The three main dumps are characterized by different element association and Coren del Cucì shows the highest As content (mean value = 868 mg/kg). Even if there is not evidence of AMD processes that can lead to a strong mobilization of metals from solid phases to waters, a campaign of sampling, analysis and geochemical characterization of natural waters circulating in the area is in progress, since superficial and groundwaters are the main natural vehicle of transport of PTE.

Plant data set showed that *C. vulgaris* and *D. filix-mas* are metal-tolerant species that can colonize and reproduce on metal contaminated soils, even if they can not be considered as hyperaccumulators. These plants behave as excluders and accumulation occurs only in roots, where internal metal detoxification mechanisms might exist in addition to exclusion strategies. So, they can be used surely as slope dump “stabilizators”.

C. *vulgaris* is able to grow on acid, ore-characterized and nutrients-poor substrates and can be a reliable marker for this kind of soils. This species can tolerate high concentration of metals and As by avoiding element accumulation in the aboveground biomass and reducing the bioavailability of these hazardous pollutants in the environment. This species appears interesting for mine land restoration and soil stabilization of Cu, Zn, Pb, Ni, Cd and As due to: a) its capability to tolerate high levels of eco-toxic elements, with minimal carriage to the aerial part; b) its partnership with ERM fungi, that plays an important role in metal tolerance and nutrient balance. More studies regarding pollutant bioavailability and phytostabilisation project feasibility are needed.

Chapter 6

Concluding remarks

The determination of PTE environmental impacts at mine lands is a complex issues, since it regards different environmental matrix, as earth material (soils and waste-rocks), superficial and underground waters and also living beings. All of these can be investigated by biogeochemical tools, as they are very useful to understand how PTE move from waste-rocks to the surrounding ecosystems and how a careful mine land management can control their impacts.

In this study, geochemical characterisation of mine dumps allowed to identify different types of waste-rocks, with different chemical features. Different significant environmental parameters (regarding pH values, AMD generation potential, PTE concentrations and their geochemical mobility) can be occurred in the same dump. As a matter of facts, this study showed that to consider each dump as a homogeneous body can be misleading, as they can be characterised by a high degree of geochemical spatial variability. This analysis is necessary in the following step that concerns the geochemical hazard/risk assessment and could be also useful later, during the remediation planning.

At Hop waste-rock dump (Rosia Montana mine site, Romania) this spatial heterogeneity is well represented. Earth material is composed by two different rock types: (1) the so-called WR1 samples, a source of acid drainage ; and (2) the WR2 samples, able to buffer the production of acidic water. On the whole, Hop waste rock dump is however a source of acid drainage, as showed both by static and kinetic tests. These last have confirmed to be an important tools for geochemical assessment of abandoned mine-waste dumps, as they are a quick, cost-effective and qualitative leach procedure to evaluate the impact of contaminated earth material on groundwater and to assess metal mobilisation from waste-rocks.

The case of Hop waste-rock dump outlines that a more accurate management of waste materials could have prevented AMD processes and the subsequent leaching of heavy metals. The concentrations of PTE into the waste rocks are generally below the regulatory limits, with the exception of As, which has concentrations up to 10 times higher than those prescribed by law, so deserving particular attention.

A more accurate management of waste materials should be necessary also at Gromo-Gandellino mine site, where the occurrence of waste-rock dumps represents an environmental hazard for the area: soil heavy metal concentrations is about one order of magnitude higher than in natural soils, specially at Coren del Cucì site.

The relationships between earth materials and plant species growing on waste-rock dumps can be also investigated using biogeochemical tools, in order to collect useful information regarding mine land rehabilitation and phytoremediation purposes.

This study confirmed that the tree species growing on Hop waste-rock dump, belonging to *Salix* spp., *B. pendula* and *P. tremula,* are able to tolerate limiting conditions (such as acid pH values and mean As content of 80 mg/kg), as known from the literature. They actively accumulate Cu and Zn in their tissues, specially in leaves, although they can not be considered as hyper-accumulators. On the other hand, the same species act as excluders for As, whose concentration in plant tissues are lower than in soils, exceeding however toxic values. These data suggest that an exclusion metal-tolerance strategy may work in synergy with physiological detoxification mechanisms. In particular*, Salix* spp. represents the species more able to tolerate different environmental situations and to grow on strong acid substrates, acting as a pioneer species that could be used for revegetation of mine lands and stabilization of dump slopes, even on the area still not vegetated. However, these species accumulate eco-toxic elements in their leaves, such as Cu and Zn, that are actually moving from substrates to living beings, with a potential geochemical hazard.

On the other hand, Gromo-Gandellino mining area is colonised by the metal tolerant species *C. vulgaris* and *D. filix-mas*. These plants behave as excluders and accumulation occurs only in roots, where internal metal detoxification mechanisms might exist in addition to exclusion strategies. So, they can be used surely as slope dump “stabilizators” and, in particular, *C. vulgaris* appears interesting for mine land restoration and soil stabilization of Cu, Zn, Pb, Ni, Cd and As.

In conclusion, the biogeochemical characterisation of mine lands give useful information to support their management, as it can provide information for the choice of sites that need priority remediation activities, and identify, within these sites, the areas responsible for contamination. Moreover, the identification of metal tolerance species and their strategies can provide useful information for project of rehabilitation, but can also highlight how PTE move through food webs.

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Appendix A

Rosia Montana mining area data

APPENDIX A.1:

UTM coordinates, grain size and color features of waste rocks

	UTM coordinates			Grain Size			Color	
Sample ID	**X**	**Y**	**WR class**	**< 2mm**	**D50**	**D90/ D10**	**Hue**	**Val/Chr**
				%	**mm**	**-**		
A2	663225	5128898	WR1	37.0	3.10	33.91	5.0 YR	3/1
A3	663226	5128925	WR1	39.0	3.39	87.17	10.0 YR	8/4
A4	663220	5128960	WR1	29.8	4.00	52.46	7.5 YR	4/6
A5	663221	5128993	WR2	37.7	3.28	63.33	2.5 Y	5/1
A6	663220	5128020	WR2	53.1	1.79	27.58	10.0 YR	5/1
B1	663250	5128870	WR2	69.2	2.02	58.63	2.5 Y	4/1
B2	663250	5128900	WR2	62.2	1.07	15.95	2.5 Y	4/1
B3	663250	5128930	WR1	43.2	2.53	56.36	2.5 Y	7/1
B4	663250	5128960	WR1	37.4	3.43	61.76	2.5 Y	8/4
B5	663250	5128990	WR1	32.2	3.67	51.75	10.0 R	6/4
B6	663250	5128020	WR1	36.2	3.22	63.69	10.0 YR	6/4
B7	663250	5128050	WR2	53.4	1.76	52.34	5.0 YR	5/1
C2	663280	5128900	WR1	74.4	0.87	25.62	7.5 YR	4/6
C3	663280	5128930	WR1	41.8	2.95	80.89	2.5 Y	8/3
C4	663278	5128957	WR1	31.9	5.24	174.78	10.0 YR	5/6
C5	663274	5128989	WR1	36.5	3.07	54.58	10.0 YR	5/6
C6	663280	5128020	WR1	59.3	1.52	19.97	10.0 YR	4/3
C7	663280	5128050	WR2	55.9	2.29	57.88	2.5 Y	4/1
D3	663210	5128930	WR1	32.4	3.32	27.75	10.0 YR	4/3
D4	663210	5128960	WR1	24.3	4.60	33.93	10.0 YR	7/2
D5	663210	5128990	WR1	272	5.15	87.27	7.5 YR	4/4
D6	663210	5128020	WR2	55.7	1.64	90.92	2.5 YR	4/1
E1	663220	5128845	WR1	24.3	5.23	49.11	2.5 Y	7/6
E2	663250	5128840	WR2	61.9	1.15	91.86	2.5 YR	4/1
E3	663282	5128854	WR1	55.6	1.57	78.26	10.0 YR	06/06/13

APPENDIX A.2:

Chemical composition (major and minor elements), LOI and sulfur content of waste rocks as wt%.

Sample ID	WR class	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	LOI	S
A2	WR1	63.47	18.34	0.45	3.67	1.04	0.43	0.17	7.10	0.17	0.11	5.16	0.81
A3	WR1	62.41	21.25	0.41	3.17	0.96	0.02	0.25	8.10	0.04	0.13	4.79	0.15
A4	WR1	56.84	20.11	0.49	6.56	1.50	1.49	0.15	7.60	0.23	0.18	5.91	2.04
A5	WR2	52.65	19.89	0.69	6.38	3.01	4.62	1.18	5.77	0.55	0.12	7.44	0.73
A6	WR2	52.88	19.45	0.67	5.38	2.64	5.43	1.46	6.04	0.39	0.12	8.10	1.49
B1	WR2	52.06	19.38	0.71	6.17	3.27	6.28	2.13	4.35	0.19	0.12	7.56	0.41
B2	WR2	58.33	18.43	0.49	4.46	2.22	3.98	0.79	5.04	0.35	0.11	7.27	1.06
B3	WR1	60.46	19.92	0.41	4.12	1.01	0.61	0.32	6.82	0.03	0.19	6.83	1.83
B4	WR1	62.81	21.48	0.41	2.30	0.90	0.03	0.55	6.85	0.02	0.13	5.24	0.01
B5	WR1	59.72	20.23	0.44	3.70	1.37	1.21	0.37	8.10	0.10	0.18	5.55	0.60
B6	WR1	61.03	19.00	0.56	4.00	0.93	0.37	0.39	8.91	0.05	0.11	5.35	1.42
B7	WR2	50.04	19.54	0.63	6.76	3.81	7.00	2.10	3.83	0.19	0.11	8.48	0.43
C2	WR1	57.84	17.28	0.53	9.04	0.94	0.25	0.14	6.94	0.09	0.35	7.49	2.07
C3	WR1	60.01	18.29	0.36	5.30	1.02	0.07	0.18	8.63	0.05	0.18	6.86	1.73
C4	WR1	60.78	17.87	0.47	6.50	0.89	0.14	0.55	7.45	0.05	0.20	6.07	0.99
C5	WR1	58.81	20.30	0.45	3.88	1.03	0.38	0.46	7.12	0.05	0.15	8.66	1.08
C6	WR1	55.86	19.86	0.54	6.35	1.26	1.43	0.62	6.89	0.37	0.19	7.85	1.86
C7	WR2	50.31	19.34	0.68	6.42	4.22	6.42	1.93	5.25	0.25	0.12	7.62	0.35
D3	WR1	57.82	20.86	0.50	5.96	1.60	0.50	0.20	6.54	0.50	0.17	6.44	0.68

APPENDIX A.2:

Chemical composition (major and minor elements), LOI and sulfur content of waste rocks as wt%.

Continue

Sample ID	WR class	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	P_2O_5	LOI	S
D4	WR1	57.86	22.64	0.50	2.64	1.80	0.28	0.14	8.40	0.29	0.09	6.16	1.42
D5	WR1	56.58	19.42	0.57	6.15	1.59	1.40	0.56	7.43	0.20	0.17	7.24	1.48
D6	WR2	51.88	20.70	0.67	5.07	2.48	4.59	1.12	5.92	0.42	0.13	8.13	0.66
E1	WR1	62.33	21.87	0.39	2.07	1.01	0.01	0.13	8.17	0.03	0.08	4.45	0.30
E2	WR2	51.99	17.67	0.70	6.02	3.20	6.59	1.96	4.87	0.22	0.14	7.67	1.14
E3	WR1	63.80	18.52	0.49	4.16	0.96	0.13	0.61	6.96	0.06	0.13	4.69	0.46
WR1	**Mean**	**60.19**	**19.81**	**0.47**	**4.63**	**1.14**	**0.41**	**0.32**	**7.53**	**0.12**	**0.16**	**6.09**	**1.10**
	Max value	63.80	22.64	0.57	9.04	1.80	1.49	0.61	8.91	0.50	0.35	8.66	2.07
	Min value	56.58	17.28	0.36	2.07	0.89	0.01	0.13	6.54	0.02	0.08	4.45	0.01
WR2	**Mean**	**51.69**	**19.42**	**0.67**	**6.03**	**3.23**	**5.85**	**1.70**	**5.15**	**0.32**	**0.12**	**7.86**	**0.74**
	Max value	52.88	20.70	0.71	6.76	4.22	7.00	2.13	6.04	0.55	0.14	8.48	1.49
	Min value	50.04	17.67	0.63	5.07	2.48	4.59	1.12	3.83	0.19	0.11	7.44	0.35
94-25 fresh[1]		*58.54*	*18.36*	*0.59*	*5.16*	*2.37*	*6.53*	*3.37*	*01.24 .00*	*0.13*	*0.19*	*2.85*	*n.a.*
94-23 altered[1]		*60.15*	*18.42*	*0.61*	*4.49*	*0.86*	*1.26*	*0.03*	*5.07*	*0.16*	*0.17*	*7.71*	*n.a.*

[1] data from Alderton et al. (2000); n.a.= not analyzed

APPENDIX A.3:

Selected trace element content of waste rocks and geochemical features of leached waters

		Earth material												Leached water					
Sample ID	**WR class**	**Ba**	**Rb**	**Sr**	**V**	**Y**	**Zr**	**Ag**	**As**	**Cu**	**Ni**	**Pb**	**Zn**	**pH**	**EC**	**SO_4^{2-}**	**Cu**	**Zn**	**As**
		mg/kg													µS/cm	mg/kg	µg/kg	µg/kg	µg/kg
A2	WR1	390.5	270.3	61.0	83.6	7.6	181.3	2.1	80.3	46.7	4.4	43.6	30.6	3.45	330	103	99	326	2
A3	WR1	368.2	316.7	66.1	79.6	17.5	166.7	6.6	123.4	28.5	1.2	36.6	22.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A4	WR1	429.9	264.0	47.1	109.8	10.2	185.3	3.7	103.9	36.6	7.2	46.4	77.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
A5	WR2	352.0	196.0	84.9	167.6	21.9	195.6	2.3	66.0	51.4	10.3	32.3	98.9	7.52	386	14	3	51	7
A6	WR2	313.7	205.7	90.0	150.9	20.2	205.4	1.7	59.8	41.2	9.4	22.7	75.1	8.34	371	90	0	122	2
B1	WR2	254.7	170.7	128.3	160.2	22.6	207.8	0.2	50.0	46.5	8.1	26.6	81.6	8.97	78	14	1	70	4
B2	WR2	297.1	182.4	71.1	114.5	22.5	193.4	1.2	75.5	54.8	12.4	36.1	85.3	7.19	904	28	2	178	4
B3	WR1	452.1	265.3	67.6	94.5	16.1	172.5	1.0	109.1	23.9	2.5	40.7	44.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B4	WR1	490.4	289.2	56.9	94.2	17.9	170.7	1.1	111.7	17.6	1.4	30.6	10.2	4.68	27	32	1	111	1
B5	WR1	542.1	306.4	85.5	98.0	11.6	180.7	2.6	148.3	32.2	3.7	36.6	32.2	7.24	173	185	2	131	2
B6	WR1	452.7	302.8	80.1	124.8	9.4	194.2	13.9	109.8	24.0	0.8	88.4	20.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
B7	WR2	255.8	149.7	137.6	170.0	23.4	201.3	0.0	46.7	48.3	8.2	22.2	72.7	8.45	96	168	0	22	2
C2	WR1	327.4	205.6	69.1	111.8	9.5	157.3	3.1	166.3	32.0	3.5	30.3	35.7	2.95	492	13	66	255	1
C3	WR1	559.7	298.1	58.7	79.4	6.4	157.9	4.0	231.0	21.1	1.4	40.6	43.2	4.16	54	475	3	149	1
C4	WR1	392.1	242.9	81.0	102.7	11.2	171.2	13.3	132.1	31.4	1.6	43.5	46.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
C5	WR1	492.3	279.4	68.2	94.3	10.2	178.1	2.3	123.1	32.3	2.4	47.4	43.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

APPENDIX A.3:

Selected trace element content of waste rocks and geochemical features of leached waters

Continue

		Earth material												Leached water					
Sample ID	**WR class**	**Ba**	**Rb**	**Sr**	**V**	**Y**	**Zr**	**Ag**	**As**	**Cu**	**Ni**	**Pb**	**Zn**	**pH**	**EC**	**SO_4^{2-}**	**Cu**	**Zn**	**As**
		mg/kg													µS/cm	mg/kg	µg/kg	µg/kg	µg/kg
C7	WR2	315.0	184.7	141.2	174.1	21.8	211.3	0.7	52.0	52.6	9.0	48.1	204.4	8.83	91	21	0	44	1
D3	WR1	49.4	243.3	36.0	114.8	19.1	184.9	3.1	112.1	60.6	13.4	45.1	114.7	4.37	657	16	42	570	2
D4	WR1	432.8	356.8	30.9	105.4	15.5	205.4	3.5	79.2	21.0	1.1	36.2	68.8	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
D5	WR1	359.4	253.5	74.4	137.9	10.9	187.6	3.8	100.4	39.0	4.8	29.3	85.7	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
D6	WR2	340.0	221.8	86.0	160.0	20.8	189.9	1.5	88.2	39.9	9.6	31.5	115.2	8.60	115	25	0	83	2
E1	WR1	518.6	340.0	39.4	77.5	11.5	176.5	1.7	72.7	11.6	2.3	46.7	36.9	3.30	195	14	4	125	4
E2	WR2	218.1	187.0	157.9	144.4	21.1	212.4	5.7	55.4	51.4	8.3	24.5	108.7	8.46	96	119	1	97	2
E3	WR1	465.9	247.9	77.6	89.5	6.2	182.9	1.6	107.1	29.5	2.3	31.5	44.0	3.42	188	370	18	266	1
WR1mean		**412.1**	**278.4**	**60.9**	**100.0**	**11.9**	**178.2**	**4.3**	**117.5**	**30.4**	**3.4**	**42.5**	**48.3**	**3.70**	**214**	**47**	**32**	**205**	**3**
WR2 mean		**292.8**	**187.9**	**118.0**	**161.0**	**21.7**	**203.4**	**1.7**	**59.7**	**47.3**	**9.0**	**29.7**	**108.1**	**8.20**	**257**	**107**	**2**	**88**	**2**
94-25 fresh[1]		506.0	40.0	533.0	141.0	21.0	104.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
94-23 altered[1]		616.0	253.0	29.0	139.0	13.0	95.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

[1] data from Alderton et al. (2000); n.a.= not analyzed

APPENDIX A.4

Screening tools (pH and EC), AMD static test and mineralogical analyses

Sample ID	WR class	Screening tools		MPA	ANC	NAPP	Silic.	Sulf.	Carb.	Other	Sec. min.
		pH	EC				Primary minerals				Authigenic
			µS/cm	kg H_2SO_4/t	kg H_2SO_4/t	kg H_2SO_4/t	%	%	%	%	%
A2	WR1	4.05	1,240	24.79	0.00	24.79	82.60	4.80	0.00	0.80	11.80
A3	WR1	4.65	170	4.59	0.00	4.59	84.50	1.80	0.00	1.50	12.20
A4	WR1	3.21	2,550	62.42	0.00	62.42	71.00	13.50	0.00	0.50	15.00
A5	WR2	7.52	1,824	22.34	78.28	-55.94	61.20	4.80	21.20	0.70	12.10
A6	WR2	7.73	1,882	45.59	85.25	-39.66	59.10	7.50	21.80	0.50	11.10
B1	WR2	8.21	384	12.55	91.69	-79.14	61.30	2.90	22.80	1.00	12.00
B2	WR2	7.72	1,890	32.44	71.26	-38.82	62.60	5.90	20.80	0.50	10.20
B3	WR1	3.17	1,684	56.00	0.00	56.00	78.00	11.50	0.00	0.00	10.50
B4	WR1	4.98	111	0.31	0.52	-0.21	83.20	1.50	2.90	1.60	10.80
B5	WR1	7.52	925	18.36	7.59	10.77	78.90	5.20	3.90	0.50	11.50
B6	WR1	3.53	1,325	43.45	0.00	43.45	79.50	8.10	0.00	0.70	11.70
B7	WR2	8.28	440	13.16	107.77	-94.61	59.40	3.50	24.50	0.80	11.80
C2	WR1	3.00	932	63.34	0.00	63.34	65.40	13.00	0.00	0.80	20.80

Silic.= silicates, Sulf.= sulfides, Carb.= carbonates, Sec. min.= secondary minerals

APPENDIX A.4

Screening tools (pH and EC), AMD static test and mineralogical analyses

Continue

Sample ID	WR class	Screening tools		MPA	ANC	NAPP	Silic.	Sulf.	Carb.	Other	Sec. min.
		pH	EC					Primary minerals			Authigenic
			µS/cm	kg H_2SO_4/t	kg H_2SO_4/t	kg H_2SO_4/t	%	%	%	%	%
C3	WR1	4.71	253	52.94	0.00	52.94	76.60	9.70	0.00	1.20	12.50
C4	WR1	3.55	837	30.29	0.00	30.29	76.10	5.20	0.00	0.20	18.50
C5	WR1	3.61	1,053	33.05	0.00	33.05	81.50	5.80	0.00	1.20	11.50
C6	WR1	6.7	1,652	56.92	9.93	46.99	68.00	13.50	4.80	0.70	13.00
C7	WR2	8.36	388	10.71	94.90	-84.19	60.80	2.70	22.90	0.40	13.20
D3	WR1	5.2	2,120	20.81	0.58	20.22	75.20	5.70	2.20	0.00	16.90
D4	WR1	3.04	2,440	43.45	0.00	43.45	83.60	7.50	0.00	0.90	8.00
D5	WR1	5.68	2,080	45.29	0.00	45.29	76.50	7.90	0.00	0.80	14.80
D6	WR2	8.14	538	20.20	82.03	-61.84	60.80	4.60	21.50	0.50	12.60
E1	WR1	3.94	330	9.18	26.54	-17.36	78.20	3.50	10.20	0.60	7.50
E2	WR2	8.22	496	34.88	34.91	-0.03	65.10	7.50	14.70	1.20	11.50
E3	WR1	3.74	396	14.08	0.00	14.08	83.90	3.80	0.00	0.80	11.50

Silic.= silicates, Sulf.= sulfides, Carb.= carbonates, Sec. min.= secondary minerals

APPENDIX A.5

Selected PTE concentration in plant tissue, BF and TF values

Plant species and tissue°	Earth material sample	Cu	Zn	As	BF			TF			
			mg/kg		Cu	Zn	As	Tissue°	Cu	Zn	As
Salix spp.											
L	B4	34.1	401.1	25.8	1.9	39.4	0.06				
L	B5	38.9	397.5	45.1	1.2	12.3	0.10				
L	C2	39.8	418.1	30.0	1.2	11.7	0.05				
L	B2	44.5	631.5	44.6	0.8	7.4	0.12	L/B	0.7	1.5	md
B		62.8	430.1	md	1.1	5.0	md				
L	E1	20.8	301.7	25.2	1.8	8.2	0.07	L/B	1.2	1.8	1.1
B		17.0	168.2	22.5	1.5	4.6	0.06				
P. tremula											
L	B4	55.5	576.8	24.5	3.1	56.5	0.06	L/B L/R	0.7 2.1	4.4 19.5	1.0 0.8
B		27.0	29.6	32.4	1.5	2.9	0.07		2.9	4.4	0.8
R		79.5	130.3	27.6	4.5	12.8	0.06				
L	C3	94.4	275.2	30.4	4.5	6.4	0.05	L/B L/R	2.1 3.0	2.2 5.4	1.1 0.9
B		31.3	50.9	32.4	1.5	1.2	0.06	B/R	1.5	2.4	0.9
R		45.6	122.6	27.6	2.1	2.8	0.05				
B. pendula											
L	B5	67.3	1,025.9	48.4	2.1	31.8	0.11	L/B	1.5	1.8	1.4
B		63.7	251.8	23.3	2.0	7.8	0.05				
L	C3	90.5	242.2	22.8	4.3	5.6	0.04	L/B	1.1	4.1	2.1
B		58.9	136.7	20.6	2.8	3.2	0.04				
P. sylvestris											
L	N1	10.4	38.0	1.9	0.3	0.4	0.03				
L	N2	11.9	32.4	2.3	0.3	0.4	0.03				
Normal ranges in plants*		5 - 30	27 - 150	1.0-1.7							

md = missing data; ° Tissues: L = leaves; B = branches; R = roots; *Kabata-Pendias, 2011

Appendix B

Gromo - Gandellino mining area data

APPENDIX B.1 Selected PTE concentration and pH values in earth material

Sampling area N of samples		**Zn** mg/kg	**Cu** mg/kg	**Pb** mg/kg	**Co** mg/kg	**Ni** mg/kg	**Ag** mg/kg	**Cd** mg/kg	**As** mg/kg	**pH**
Coren del Cucì	max	19889.0	2861.1	7,446.0	424.0	255.0	72.0	18.1	2,092.5	6.31
N=29 mine rocks	min	50.2	39.5	114.8	15.9	8.6	0.3	0.4	9.5	4.14
	mean	**1,018.6**	**957.2**	**573.0**	**174.6**	**85.0**	**27.0**	**6.9**	**864.4**	**5.24**
	sd	3587.0	699.6	1,374.2	112.8	65.4	20.6	4.5	550.0	0.64
Coren del Cucì	max	584.6	650.8	352.1	84.6	31.3	16.2	13.4	40.,1	6.01
N=25 soils outside mine dump	min	43.1	3.4	36.8	6.1	8.6	0.2	4.5	81.3	4.07
	mean	**221.7**	**90.6**	**178.0**	**26.2**	**19.8**	**1.9**	**7.6**	**214.7**	**5.00**
	sd	184.7	125.1	80.3	16.4	6.8	3.6	2.8	97.6	0.43
Pradel	max	1,7491.0	883.3	9,771.0	105.6	121.0	111.8	53.6	67.,5	6.57
N=11	min	71.1	35.0	176.8	5.7	6.6	0.8	1.5	92.7	4.27
	mean	**3539.5**	**295.4**	**3,194.1**	**37.9**	**51.2**	**19.7**	**8.0**	**198.9**	**5.07**
	sd	6307.6	262.6	3,867.8	31.3	39.2	32.3	15.4	169.0	0.84
Vedriol	max	56.6	1,949.2	51.3	397.0	164.3	8.5	80.9	1,412.2	5.67
N=10	min	0.8	17.2	6.7	91.1	56.5	1.7	4.9	65.6	3.69
	mean	**12.4**	**311.2**	**17.2**	**218.1**	**105.5**	**3.7**	**19.9**	**444.9**	**4.58**
	sd	17.1	594.9	12.6	105.1	33.2	2.4	24.0	402.9	0.64

APPENDIX B.2

Selected PTE concentration in plant tissues and variation range of Bf and TF (a.p. aerial parts; r roots)

Plant species			PTE content (mg/kg)							**BF**							**TF** (leaves)						
Sampling area			**Zn**	**Cu**	**Pb**	**Co**	**Ni**	**Cd**	**As**	**Zn**	**Cu**	**Pb**	**Co**	**Ni**	**Cd**	**As**	**Zn**	**Cu**	**Pb**	**Co**	**Ni**	**Cd**	**As**
C. vulgaris	N=12 a.p.	max	138.5	53.1	38.2	10.4	25.9	12.0	38.1	1.26	0.06	0.28	0.13	1.01	2.90	0.02	0.7	0.0	0.3	0.3	0.6	1.3	0.1
Coren del Cucì		min	43.3	11.2	18.4	0.1	7.6	0.2	2.5	0.22	0.01	0.06	0.01	0.20	0.02	0.00	0.5	0.0	0.2	0.1	0.4	0.1	0.0
		mean	**80.2**	**25.8**	**26.9**	**5.1**	**14.3**	**6.5**	**9.8**														
	N= 3 r.	max	137.6	1313.0	148.8	123.4	30.9	21.2	279.8	2.37	1.33	0.80	1.09	1.62	1.91	0.28							
		min	123.0	206.3	91.8	10.7	19.6	8.7	39.7	0.70	0.48	0.76	0.16	0.67	1.05	0.08							
		mean	**129.3**	**858.5**	**125.9**	**57.8**	**27.1**	**17.0**	**148.7**														
GRO-08	a.p.		31.7	5.8	3.5	n.d.	1.6	n.d.	0.5	0.38	0.12	0.02	n.d.	0.10	n.d.	0.01	0.4	0.6	0.1	n.d.	0.5	n.d.	0.7
	r.		70.0	9.7	34.4	n.d.	3.2	n.d.	0.7	0.83	0.21	0.22	n.d.	0.22	n.d.	0.01							
D. filix mas	N=4 a.p.	max	75.0	25.2	8.6	4.5	4.7	n.d.	3.5	1.05	0.26	n.d.	0.20	0.38	n.d.	0.04	0.5	0.7	n.d.	n.d.	1.0	n.d.	0.8
Pradel		min	43.6	18.3	0.0	0.0	1.2	n.d.	1.0	0.23	0.03	n.d.	0.01	0.05	n.d.	0.01	0.3	0.2	0.2	n.d.	0.7	n.d.	0.0
		mean	**64.7**	**22.4**	**<10**	**1.3**	**2.7**	n.d.	**2.0**														
	N=3 r.	max	126.4	29.9	77.5	2.0	45.3	n.d.	7.2	0.82	0.55	0.38	0.06	2.63	n.d.	0.06							
		min	79.2	25.6	45.6	1.1	8.9	n.d.	6.1	0.72	0.03	0.11	0.02	0.20	n.d.	0.01							
		mean	**102.8**	**27.7**	**61.6**	**1.6**	**27.1**	n.d.	**6.6**														

APPENDIX B.2

Selected PTE concentration in plant tissues and variation range of Bf and TF (a.p. aerial parts; r roots)

Continue

Plant species			PTE content (mg/kg)							**BF**							**TF** (leaves)						
Sampling area			**Zn**	**Cu**	**Pb**	**Co**	**Ni**	**Cd**	**As**	**Zn**	**Cu**	**Pb**	**Co**	**Ni**	**Cd**	**As**	**Zn**	**Cu**	**Pb**	**Co**	**Ni**	**Cd**	**As**
D. filix mas	N=10 a.p.	max	141.1	57.1	60.8	1.5	7.6	0.7	36.4	1.46	0.87	0.29	0.11	0.44	0.26	0.07	0.8	3.7	n.d.	n.d.	1.9	n.d.	0.9
Vedriol		min	21.1	14.5	0.0	0.0	0.6	0.0	0.8	0.21	0.03	0.04	0.06	0.10	0.17	0.00	0.4	0.6	n.d.	n.d.	1.1	n.d.	0.7
		mean	**57.9**	**27.0**	**28.3**	**1.0**	**3.8**	**0.6**	**10.8**														
	N= 4 r.	max	142.6	153.8	94.5	8.1	10.1	2.2	295.3	1.38	0.51	0.24	0.31	0.35	0.21	0.21							
		min	81.9	22.3	31.1	1.4	3.3	0.7	2.9	0.50	0.07	0.13	0.10	0.20	0.08	0.01							
		mean	**114.3**	**83.5**	**52.9**	**4.0**	**6.2**	**0.7**	**100.2**														
GRO-08	a.p.		46.9	18.7	<10	<0.4	<0.5	n.d.	0.7	0.56	0.40	n.d.	0.00	0.04	n.d.	0.01	1.1	0.7	n.d.	n.d.	n.d.	n.d.	0.5
	r.		41.7	25.7	37.6	0.4	2.5	n.d.	1.3	0.49	0.55	0.24	0.05	0.17	n.d.	0.02							

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