Chapter 5
Potentially Harmful Elements in Abandoned Mine Waste

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Abstract Soils are essential components of the environment therefore; soil quality must be controlled and preserved. However, the increased concentration and distribution of potentially toxic elements (PTE) in soils by anthropogenic activities of industrial and mining resources are causing worldwide concern. The anomalous concentration of PTE may affect the soil's environment, reducing it's quality and therefore pollution which can be followed by an eventual accumulation through the food chain. This implies a serious risk for crops, livestock and human health. There is an increasing need to apply innovative technologies of prevention, monitoring, risk assessment and remediation, more sustainable and economical, in the context of mining site soils.

In this chapter, the impact of PHEs from abandoned mine sites on the environment is discussed through case studies from Europe (NE Italy). The environmental effects recognized for these specific sites could be valid other mining sites worldwide. Some case studies highlight the toxicity assessment of contaminated soils from abandoned mining areas; others focus on the metal uptake and translocation ability in plants that can produce adverse effects on plant morphology and health and biological soil quality evaluation of abandoned mining site.

Keywords Potentially toxic elements • Mine waste • Spolic Technosols • Accumulator plants • Phytoremediation • Soil quality

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1 Introduction

Soil is a key resource for the life of organisms in terrestrial environments; it is the basis of the ecosystem and of our farming system of food production (Chesworth 2008). It is imperative to acknowledge that current and future exploitation of mineral resources will produce even more wastes and impose more threats on Earth. Pollution of soil with Potentially Harmful Elements (PHEs) is a major concern worldwide since it can cause the transfer of contaminants to other environmental compartments, such as surface water, groundwater and biota, with a consequent spread of pollution over a wider area than the initial one (Lal 2006). PHEs in the soil can be partly absorbed by the plants that derive nutrients from that soil, with the risk of accumulation and toxic effects along the food chain and also to humans (Markert et al. 2003).

Mining is only one of the pathways by which metals enter the environment. Mining itself affects relatively small areas, and this could not pose severe environmental problems. The environmental impact arises when ores are mined, milled and smelted, and a certain amount of metals is released in the surrounding areas and to waterways. Depending on the nature of the waste rock and tailings deposits, a wide dispersion of the metals both in solution and in particulate form is possible. A consequence of the high content of toxic heavy metals, in combination with reduced soil thickness, leads to discontinuous vegetation coverage that is composed mainly of crust lichens, mosses, fescue and wild vegetation genetically tolerant to high metal concentrations (Wahsha et al. 2012b).

Plants may be classified into three groups on the basis of their ability to accumulate metals in their aerial parts (Baker and Brooks 1989) Excluders are those plants whose metal concentrations remain unaffected by metal contents in soils up to a critical level, when toxic symptoms appear; Indicator plants are those whose metal concentrations reflect those the related soil; Accumulator plants have the ability to take up and concentrate metals from soils, independently on levels of metal concentrations. Among the species that may tolerate high metal concentrations in their tissues, plants presenting exceptional accumulating ability are referred to as hyperaccumulators.

2 PHEs Contamination in Soil

Soils are presently contaminated with PHEs, which are originated from different sources in particular by heavy metals, which can negatively affect soil's chemical, physical and biological properties worldwide. In this context, heavy metals can be added to the soil through diverse natural or/and anthropogenic sources. The major natural sources of heavy metals in soils are: weathering (such as soil erosion and deposition of windblown dust and running water); volcanic eruptions and bushfire.

The major anthropogenic input of heavy metals to soils mainly occurs by: Atmospheric deposition, result from energy production, power generation emissions, metal mining, smelting of metalliferous ores and manufacturing, waste and wood burning; sewage sludge, municipal and organic wastes and co-products from agriculture and food industries; Land disposal of industrial waste; Fertilizer and pesticide (insecticides, herbicides, fungicides) and soil heavy metal pollution through chemical and biological warfare (Wahsha et al. 2012d; Alloway 1995).

The environment is rather strongly influenced by manmade activities through heavy mining, especially in areas where low-grade metal ores are being extracted, which produces higher quantities of soil wastes (e.g. Heavy metals).

Heavy metals found in soils are originated from different sources. In some places we can find natural forms of contamination, due to the presence of particular rock types, such as serpentinites (Ghaderian et al. 2007). In other places, anthropogenic metal accumulation is recorded (Zhang et al. 2009). Indeed, human activity is considered to be the major source of pollution by heavy metals in soils. Among the various causes of this type of contamination we can mention mining and processing of metals, which are linked to generate several environmental problems (e.g. acid mine drainage, impacts on the landscape, pollution of water, soil removal and pollution). The ever-increasing demand for metals lead to more mining and, therefore, to larger amounts of waste production. Accessing mined produces is always accompanied by excavation of range volumes of waste rocks, whose disposal is another important problem of mining. However, little attention has been paid to processing and disposal of mining waste, which have been generally dumped on the ground, to become a potential source of pollution (Lottermoser 2010; Lal 2006; Selim and Sparks 2001).

Dispersal pattern of mine spoils can be recognised by mining activity. The effect of these irregular anthropogenic deposits is the development of a new soil material that covers the original one. Immature Entisols (Lithic Spolic Xerorthents and Spolic Xerorthents,) are formed on mine spoils <100 year old. These soils are characterized by a thin solum (<30 cm), little organic matter accumulation (mean 14 g/kg organic carbon, range 1–33 g/kg), dark brown (10YR3/3) to reddish (5YR4/6) colour, coarse texture (sandy loam to loamy), and subalkaline pH (mean 7.4, range 6.9–7.8). Detailed descriptions of soil properties of a selected profile on mine waste are given in Table 5.1.

Soils developed on old mine dumps or in the proximal parts (<0.5 km) of the dumps, have a >50 cm thick solum, sandy loam to loam texture, blocky structure, slightly acidic pH (mean value 6.3, range 4.9–7.7), humus accumulation (up to 14 % organic matter in the A horizon), moderate to low cation exchange capacity (CEC) (mean 20 $cmol_c\ kg^{-1}$), with significant desaturation (base saturation <60 %). As a rule, they have distinct A-B-C horizonation and a well formed cambic horizon. Thus, they are Inceptisols *Spolic Haploxerepts* or *Spolic Dystroxerepts*, (Table 5.2). Frequently, a discontinuity occurs between the upper and the lower portions of the profile, which developed from the underlying bedrock. Data (not reported) indicate relevant differences and a remarkable polycyclic evolution, due to the superposition of mine spoil over the normal soil. Colour,

Table 5.1 Selected properties of the Spolic Technosols

	Particle size distribution %				Organic carbon	Cation exchange capacity (CEC)
Horizon	Silt	Clay	Sand	pH	g/kg	($cmol_c\ kg^{-1}$)
A1	47	10	43	7.6	8	11.0
A2	46	9	45	7.4	4	9.0
B1	50	8	42	7.5	2	7.1
B2	48	9	43	7.7	–	9.0
2BC	57	8	35	7.8	–	17.7

texture, reaction, and CEC are the most prominent features that present important differences in soils. Soil horizons show dark brown (7.5YR3/2) to dark reddish brown (5YR 3/3) colour, well individualized structure, from crumby to fine blocky beds. Texture is coarse (sandy loam to loam) in surface horizons of mine spoils and loamy to clayey underneath. Values of pH around 6.3 at the surface indicate a soil reaction that is slightly acidic; this is slightly subalkaline (pH 7.4) and base-saturated at the bottom. Cation exchange capacity increases with depth, from 15 to 25 cmol (+)/kg (Bini 2010).

Shrubby vegetation with shallow trees (i.e. holm-oak, strawberry tree, heath, etc.) is the typical flora of these sites, where rock-rose is the dominant plant.

Far from the mine dumps (>0.5 km) the soil samples show little evidence of mine spoil in the profile. Sulphide minerals are found especially at the surface, as revealed by mineralogical and chemical investigation (Bini 2012). An abrupt textural change (Table 5.3) indicates a marked discontinuity between the upper and lower part of the soil profile. The upper part (A and E horizons) has dark brown (10YR2/2) to yellowish brown (7.5YR3/4) colours, loam to sandy loam texture, crumby structure, high organic carbon content (mean 21 g/kg), and subalkaline pH. The lower part (Bt horizon) presents reddish colours (5YR3/4–2.5YR3/4), a strong clay content increase (clay loam to clayey texture), organic carbon decreases; pH is subalkaline with traces of carbonate. Therefore, they are classified as Alfisols. Since there is evidence for mine waste in the profile, these soils should be classified as *Spolic Rhodoxeralfs or Spolic Haploxeralfs*. However, considering the net discontinuity already mentioned, these soils could be classified as *Spolic Xerorthent over Typic Rhodoxeralf* (or *Haploxeralf*) (Bini 2012).

3 Mine Soils Pollution

The availability of resources from mining sites is not an easy task, where some products are existing in almost in 100 % of the excavated sites, such as the production of sand, clay and gravel, while other products such as gold are barely reaching few parts per million of the raw material, therefore generating large volumes of wastes. Copper, zinc, and gold mining goes through several processes; such as grinding, washing, and sizes of the raw material of rocks, which generates

Table 5.2 Selected properties of the Spolic Dystroxerept

	Depth	Particle size distribution %				Organic carbon	Organic matter	CEC	Base saturation
Horizon	cm	Silt	Clay	Sand	pH	g/kg	g/kg	cmol(+)/kg	%
A1	0–47	34.7	15.3	50	6.4	27	46	25.5	62
A2	47–70	33.3	15.1	51.6	6.3	21	36	15.4	47
Bw	70–90	30.8	11.1	58.1	6.2	8	13	13.0	58

Table 5.3 Selected properties of the Spolic Haploxeralf

	Depth	Particle size distribution %				Carbonate	O. C.	Organic matter	CEC
Horizon	cm	Silt	Clay	Sand	pH	g/kg	g/kg	g/kg	cmol(+)/Kg
A1	0–3	23.9	9.5	66.6	7.6	0	23	40	29.5
A2	3–15	29.8	13.7	56.5	7.7	0	19	33	37
E	15–40	35.7	9.9	54.4	7.9	0	6	11	33
Bt_1	40–110	40.7	40.3	19	8.0	4.1	7	12	19
Bt_2	110–120	39.9	30	30.7	8.0	58	11	19	23

some byproducts such as dust and other fine-grained material, the later could be used as natural fertilizers. In general, forma mining is always producing volumes of waste material known as "gangue". Of the processes with such large volumes of mining wastes, ranked from high waste to low are coal, non-ferrous ores, ferrous ones, and industrial minerals. The type and magnitude of the released contaminants from mining sites is controlled by many factors, such as the geology, topology and climate of the mined sites, and the techniques applied for mining and processing of the mined resources. Understanding all these factors should be deemed critically important for better control of waste discharge from mining areas. Improper operations of mining activities have been facing increasingly strong criticism by environmentalists (Lottermoser 2010).

Both physical and chemical processes work during rock alteration. Physical processes appear to be a leading role during the initial stages. Steep morphology areas, where most mining districts are located, are the most affected by these processes. Loose and coarse-grained material forms as a consequence of rock fragmentation. Rock fragments migration on instable slopes, erosion of fine particles by wind plus runoff, all these processes contribute to land modelling.

The rock transformations also occur by chemical processes such as oxidation potential (Eh >250 mV), acidification (pH <7), hydrolysis, metal leaching, precipitation of oxy-hydroxides and sulphates, argillogenesis. Wet and high temperature climatic conditions increase the role of chemical processes and stimulate mine waste reactivity. Thus, the physical and chemical processes of soils developed from mine soils lead to new soils with a different set of physical and chemical features.

The formation of a biologically active substrate may occur as the parent material is finely subdivided and weathered, and this permits the development of a pioneer vegetation (lichens, mosses). Litter accumulation (OL horizon) is the process that characterizes the early stage of soil formation. Subsequently, organic matter decomposition (OF horizon), humus formation (OH horizon), mineralisation (A horizon) constitute a first pedogenetic phase (Bini 2012, 2010). According to Jabiol et al. (2007), this phase may bring to the differentiation of several types of humus as a function of litter composition, microflora and microfauna activity, pH and climate conditions.

A second pedogenetic phase is determined by *in situ* mineral transformations (e.g. acid hydrolysis), oxyhydroxides and clay formation (stage of *cambic* horizon formation). In this phase, colour varies from very dark brown (10YR 3/3) to dark brown (7,5YR 3/3), reddish brown (2,5YR 3/2), dark yellowish brown (10YR 4/5), or blackish (5YR 2, 5/5), in relation to the nature of the bedrock, and/or to the amount of mine waste.

A third pedogenetic phase is consistent with solute leaching and particles migration towards bottom (stage of *argillic* horizon formation); precipitation of new minerals (e.g. carbonate, sulphate) is also likely to occur. However, this third phase is difficult to assess in mine waste materials. Since the time elapsed from mining operations in most cases is not sufficient for Bt formation, considering that the landscape morphology is generally undulated, with slopes ranging from 15 to 45 %, which makes erosion a dominant process. However, soils developed from waste dumps are generally shallow (20–100 cm), skeletal, coarse-textured (sandy loam to loamy sand), little developed, with limited horizonation (Bini 2007, 2012).

Mine waste production varies between countries, depending on intensity of mining activities in each country, and on methods of mining and processing (Table 5.4).

Earth's crust is noticeably enriched with different metallic and mineral compounds accumulated over time due to various geological processes. Geological processes leads to the formation of different deposits according to the amount and type of mineral enrichment in each deposit. Mineral deposits formation and differentiation is an important aspect in understanding the environment. Deposits geology (included rock composition, geomorphology etc.) may influence the characteristics of soil chemistry, surface and ground water properties leading to the natural enrichment of soils, waters, and sediments with metals and metalloids (Lottermoser 2010).

Natural enrichment of metals and metalloids varies between sites, leading to the adaptation of the covering vegetation to specific soil contaminants. For example, *serpentine flora* is the type of vegetation highly adapted to lands with overlying soils highly enriched with iron, nickel, chromium and magnesium. Soils enriched with boron favor the growth of cereal and legume crops. Soils enriched in selenium have tolerant vegetation covering, although animals grazing on such plants will suffers acute toxicity.

Accordingly, elemental enrichment in ores and rocks could cause unfavorable effects on local and regional ecosystems due to the signature of such elemental

Table 5.4 Mining waste production compared to municipal waste in different countries of the world

Country	Mining waste (Mt)	Tailing waste (Mt)	Municipal waste (Mt)
European Union	4,700	1,200	218
United States	2,000	–	200
South Africa	1,100	–	421
Australia	1,750	–	1,300
China	700	300	–

Source: Lottermoser (2010)

enrichment to surrounding water bodies, soils and sediments. Such adverse effects could result from geological processes or artificially imposed due to the improper mining practices and mine wastes disposal and management (Lottermoser 2010).

4 Environmental Impacts of Abandoned Mines, Scientific Issues and Case Studies

The impact of PHEs from abandoned mine sites on the environment will be discussed through case studies from Europe (NE Italy). The environmental effects recognised for these specific sites could be valid other mining sites worldwide.

The area we are considering is an abandoned mine site in North-East Italy called "Imperina Valley", at an altitude ranging between 543 and 990 m above sea level. The geological substrate consists of rocks of the metamorphic basement (Pre-Permian), in tectonic contact with dolomite rocks (Dolomia Principale, Upper Triassic).

The Imperina stream crosses the valley; even if no settlements can be found in this area, many buildings and tunnel outlets still witness the past mining activity. Part of the area (right side and a portion of the bottom) lies within the National Park of the Belluno Dolomites. The mined area, located along the tectonic contact between basement and dolomites, consists of a deposit of mixed sulfides, composed primarily of cupriferous pyrite, pyrite and chalcopyrite, with minor amounts of other metallic minerals (Frizzo and Ferrara 1994). Copper and sulphur were the main products extracted. Until the beginning of the twentieth century, copper was extracted and processed directly in situ through roasting, a method with a severe impact on the area due to acid rains formation and intensive wood cutting. Today, the vegetation cover is mainly constituted of mixed forests (*Abies alba* Mill., *Picea abies* (L.) H. Karst., 1881, *Fagus sylvatica* L. and *Ostrya carpinifolia* Scop.), with clearances where herbaceous and shrubby vegetation prevails over the arboreal one (Dissegna et al. 1997).

The first certain historical records indicate that mining in the Valle Imperina dates back to the first years of the fourteenth century, thanks to research funded by the Republic of Venice into the mining of copper. Very probably, the extraction of minerals had already commenced in pre-Roman times, considering the particular condition and position of the rocks and the proximity of the Agordo valley; this theory is also backed up by the large amount of items made from bronze and copper found in archaeological excavations in the whole of the Belluno valley.

A notable increase in the production of copper derives from the passage of the property rights of the mines from private hands to the Republic of Venice; in fact, initially the mine was subdivided in tunnels and "mints" owned by private individuals with obvious management problems and lack of efficiency of the mining. This passage started gradually at the end of 1,600, but it was only in 1,835 that these mines formally become public property, in the hands of the Austro-Hungarian Empire.

During the first years of the last century, the whole process was electrified, and in 1925 the new standard-gauge electric railway line allowed for the loading of the materials which had been extracted from the mine and taken to the situation by cableway.

After the First World War, production stabilised at around 50,000 tonnes a year up to the period 1940–1944. Following this period, after a first attempt to modernise the mine in the early 1950s, the condition of the mineral deposit and its exhaustion led initially to staff reductions and, finally, to the complete closure of the mine on 8 September 1962 (Wahsha et al. 2011).

4.1 Case Study 1

4.1.1 PHEs Contamination in Soils and Plants of an Abandoned Mine

Over the past decades, human activities such as metal mining and milling operations have been recognized as one of the most important sources of contamination in the environment, along with mine and mill waste water (Jung 2001; Navarro et al. 2008). Heavy metal contamination has been a serious problem in the vicinity of abandoned mine sites due to the discharge and dispersion of mine-waste materials into the ecosystem (Jung and Thornton 1996). These heavy metals have a potential to contaminate soil and water (Haque et al. 2008; Lim et al. 2008). Extraction of metals from sulphide minerals usually results in large amounts of waste materials that often contain elevated concentrations of potentially harmful metals such as Cu, Zn, Cd, and Pb (Jian-Min et al. 2007; Lee et al. 2001). The degree of heavy metal contamination around mines varies depending upon geochemical characteristics of elements and degree of mineralization of the tailing (Navarro et al. 2008). Yun-Guo et al. (2006) reported that abandoned mining sites represent significant sources of metal pollutants in water and soils and a threat to the ecosystem. These metals can be transported, dispersed and accumulated in plants and then passed through the food chain to human beings as the final consumer.

The restoration of metal-contaminated sites is one of the most important environmental issues. Soil pollution by chemicals poses serious hazards to surface and ground waters, plants and humans, and presents relevant social, sanitary and economic costs (only in the U.S. up to 250$ m^{-3} soil; Adriano et al. 1995; Bini 2010). Metal accumulation in soil diminishes soil fertility, microbial activity and plant growth (Lehoczky et al. 1996). Moreover, trace elements are very persistent, can interact with plant roots by adsorption or release from the soil particles, and therefore increase the risk of long-term soil pollution and of toxic effects on organisms (Rosselli et al. 2006).

The assessment of soil contamination by metals has been extensively carried out through plant analysis (Blaylock et al. 2003; Brooks 1998; Ernst 1996; Wenzel et al. 1993); both wild and cultivated plant species have been frequently used as (passive accumulative) bioindicators for large scale and local soil contamination (Baker 1981; Baker and Brooks 1989; Bargagli 1993; Zupan et al. 1995; Zupan et al. 2003).

In the last decades, attention has been deserved to plants as tools to clean up metal-contaminated soils by the low cost and environmental friendly technique of phytoremediation (Adriano et al. 1995; Baker et al. 2000). This technology is focused on the ability of plants to accumulate high heavy metal concentrations (up to 100 times the normal concentration) in their aerial parts (i.e. they are hyperaccumulator plants as defined by Baker 1981). The plant ability to uptake metals was firstly applied in phytomining projects (Brooks and Robinson 1998; Ernst 1993; Helios-Rybicka 1996; Mc Grath 1998; Vergnano Gambi 1992), and only successively, when environmental contamination became a global concern, it was recognized as an useful tool for remediation projects (Adriano et al. 1995; Bini 2010, 2005; Bini et al. 2000b; Mc Grath 1998; Salt et al. 1995). Indeed, tolerant or accumulator populations of higher plants may colonize naturally or even anthropogenic metal-enriched areas, accompanying the disappearance of sensitive plants. Therefore, they may be utilized in restoration of such areas. The choice of plants is a crucial aspect for the remediation techniques. Up to now, more than 400 plants that accumulate metals are reported, Brassicaceae being the family with the largest number of accumulator species (Bini 2010; Marchiol et al. 2004; Mc Grath 1998).

Heavy metal accumulation is known to produce significant physiological and biochemical responses in vascular plants (Mangabeira et al. 2001). As stated by Preeti and Tripathi (2011), there is a direct relationship between chemical characteristics of soil, heavy metals concentration and morphological and biochemical responses of plants. Yet, metabolic and physiological responses of plants to heavy metal concentration can be viewed as potentially adaptive changes of the plants during stress.

Plants growing on abandoned mine sites and naturally metal-enriched soils (e.g. serpentine soils) are of particular interest in this perspective, since they are genetically tolerant to high metal concentrations, as reported by several authors (Bini 2005; Giuliani et al. 2008; Maleci et al. 1999; Brooks 1998; Pandolfini et al. 1997; Vergnano Gambi 1992), who studied endemic serpentine flora (*Alyssum bertoloni*, *A. murale*, *Silene paradoxa*, *Stachys serpentini*, *Thymus ophioliticus*) at various sites in the world. All these authors agree that morphological, physiological and phytochemical characters of serpentine plants are strongly dependent on the substrate composition (what Jenny, in 1989, called "the serpentine syndrome"), and that they are likely metal accumulator or tolerant ecotypes.

Understanding the mechanisms of metal bioaccumulation by plants species and of metal bioreduction by microorganisms is a clue to the efficiency of phytoremediation techniques. The localization and the chemical form of metals in cells are key information for this purpose (Kidd et al. 2009; Sarret et al. 2001). After their assimilation by plants, heavy metals could interfere with metabolic processes and are potentially toxic (Lopareva-Pohu et al. 2011); phytotoxicity results in chlorosis, weak plant growth, yield depression, and may be accompanied by disorders in plant metabolism such as reduction of the meristematic zone (Maleci et al. 2001), plasmolysis and reduced chlorophyll and carotenoids production (Corradi et al. 1993). Mangabeira et al. (2001) studied the ultrastructure of different organs of tomato plants (root, stem, leaf) which showed visible symptoms of Cr toxicity, and argued that CrVI induces changes in the ultrastructure of these organs. Similar findings were reported by Vasquez et al. (1991) for Cd in vacuoles and nuclei of bean roots. Since both these metals are known to be inessential to plant nutrition, it is suggested that they are likely confined in roots by a barrier-effect as defense strategy during stress. Conversely, essential metals such as Zn and Cu are easily conveyed to the aerial parts, as reported by Fontana et al. (2010).

Among wild plants, the common dandelion (*Taraxacum officinale* Web) has received attention (Bini et al. 2000a; Królak 2003; Zupan et al. 2003; Simon et al. 1996) as bioindicator plant, and has been also suggested in remediation projects (Turuga et al. 2008), given its ability to uptake and store heavy metals in the aerial tissues. *T. officinale* is a very common species, widely diffused in Central and Southern Europe, easy to identify and greatly adaptable to every substrate (Keane et al. 2001; Malawska and Wilkomirski 2001). Moreover, this species is commonly collected to be used in cooking as fresh salad or boiled vegetable, and is used also in ethnobotany and traditional pharmacopoeia (Rosselli et al. 2006). Therefore, when grown on heavily contaminated soils, it may be potentially harmful if introduced in dietary food, as it occurs in many countries.

Previous studies of our research group (Bini et al. 2000a; Fontana et al. 2010) investigated the heavy metal concentration of soils developed from mine waste material, and the wild plants (*Plantago major, Silene dioica, Stachys alopecuros, Stellaria nemorum, Taraxacum officinale, Vaccinium myrtillus, Gymnocarpium dryopteris, Gymnocarpium robertianum, Salix caprea, Salix eleagnos, Salix purpurea*) growing on those contaminated soils, in order to determine the extent of heavy metal dispersion, and the uptake by both known and unreported metal-tolerant plant species.

In the last few years many studies have focused on the potential use of trees as a suitable vegetation cover for phytoremediation (French et al. 2006; Jensen et al. 2009). A very suitable tree for use in phytoremediation is willow (Landberg and Greger 2002). Pulford and Watson (2003) detailed the phytoremediation potential of willow in heavy metal contaminated areas. Willows have not been included in the group of hyperaccumulators of heavy metals, but on the other hand they provide potential bioindicator of pollution (Mleczek et al. 2009). However,

Table 5.5 Average concentration of PHEs in soils and plants of interest expressed as mg kg^{-1}

	Cd	Cr	Cu	Pb	Zn	Fe	
PHEs in selected soils	2.41	65.16	1,378	4,811	1,051	256,308	
Italian average	0.53	100	51	21	89	–	
International average	0.30	200	20	10	50	–	
Excessive values	5	100	100	100	250	–	
Residential limits	–	150	120	100	150	1,000	
S. purpurea	Root	5.75	2.98	23	11.3	96	250
	Leaves	2.85	3.48	28	26	231	475
S. eleagnos	Root	3.16	4	61	46	248	394
	Leaves	3.4	3.8	31	36	495	523
S. caprea	Root	4.15	3	40	519	180	621
	Leaves	1.75	2.4	33	152	300	901
T. officinale	Root	0.51	1.2	57.5	102	67	213
	Leaves	0.86	3.5	65	134	133	662

metal concentrations in willows depend on species, growth performance, root density, distribution within the soil profile and sampling period (Chehregani et al. 2009). Moreover, willow has been recently recognized as a good accumulator of heavy metals (Meers et al. 2007).

Our aim was to assess total concentration of six potentially toxic metals (Cd, Cr, Cu, Pb, Zn and Fe) in the soil and plant samples of *T. officinale* and three dominant willow species (*Salix purpurea* L., *Salix caprea* L. and *Salix eleagnos* Scop.) collected from abandoned mixed sulphide mine dumps of Imperina Valley, in order to propose these plants for phytoremediation plans (Table 5.5).

Comparing the values found with those of control levels of Angelone and Bini (1992), the total concentrations of most of the investigated metals (Cd, Cu, Pb, Zn and Fe) in the soil samples were significantly higher ($p < 0.05$), and almost above the toxicity threshold according to the Italian legislation (D.L. 152/2006).

The area is almost not contaminated by Cr, whereas there are a contamination by Zn, Cu, Pb and Fe that show high concentrations, particularly at sites affected by mining activities and ore processing.

There is a linear positive correlation between Pb, Cu, Zn and Fe (Cu/Pb 0.867; Pb/Zn 0.616; Cu/Zn 0.688; Cu/Fe 0.933). This is consistent with their calcophile geochemical behaviour, since these metals tend to form compounds with sulfur, as chalcopyrite (CuFeS2), sphalerite (ZnS) and galena (PbS), commonly found in the Imperina Valley ore deposits (Frizzo and Ferrara 1994). Cr is negatively correlated with Cu (−0.847), Pb (−0.816), Zn (−0.604) and Fe (−.0754). Conversely, Fe indicates a significant positive correlation with Pb (Fe/Pb 0.734). Furthermore, Fe it is not significantly correlated with Cd. Therefore, it is likely that most of iron in soils of the study area derives from the alteration of pyrite and chalcopyrite mineralization. For all elements, it might be that the same type of elements combination occurring in the mineralization of Imperina Valley is found in soil. This means that no element of the mineralization has been removed in a special way, since the factors of pedogenesis have acted for a some decades in the areas affected by ore processing, and thus the soil chemical characteristics still seem to be close to those of the parent material, as it was found by Bini (2005) in mine soils of Tuscany.

It is noteworthy to point out, however, that willows ability to accumulate heavy metals in different parts is independent of the species; rather, it depends on local factors as soil and pedoclimate (particularly temperature, aeration and water content) and on plant physiology and aging (Wahsha et al. 2012b). Moreover, a counteracting behavior of essential and toxic heavy metals is likely to occur as a barrier effect of the roots (Fontana et al. 2011).

The calculation of translocation factors (TF) highlights that willows translocate and accumulate metals in the aerial parts, in particular Cu (*S. purpurea* TFCu = 4.72), Pb (*S. purpurea* TFPb = 3.42), Zn (*S. caprea* TFZn = 3.48), Fe (*S. purpurea* TFFe = 1.44), and Cr (*S. purpurea* TFCr = 1.24). Most of the plant species had BCF less than one and TF more than one, although the concentration of heavy metals remained below 1,000 mg kg^{-1}. In general, metal concentrations in plants vary with plant species; plant uptake of heavy metals from soil may occur either passively with the mass flow of water into the roots, or through active transport from root cells (Kabata-Pendias 2004; Mun et al. 2008).

In this case study, the metal translocation ability, combined with rapid growth and a higher biomass than herbaceous plants, qualifies willows as good candidates for phytoremediation of polluted soils (Bini 2007). Since most of the studied willows were capable to uptake and translocate more than one metal from roots to shoots and, based on high TF values, they can be used for phytoextraction. On the other hand, Cd shows very low translocation factors in all investigated plants, and proved to be blocked in the roots, since it is known to be unessential to plants, thereby suggesting some exclusion strategy by plants (Vandecasteele et al. 2002).

Anthropic influence related to mining activity in soils of the studied area is evident. Soils in the mining site are highly contaminated by heavy metals, mainly Cu, Zn, Pb and Fe. The metal content in willows show relatively high concentrations of these elements. The results of this study indicated that there is an increasing need for further research on the mechanisms whereby such plants are able to survive in contaminated soils. Furthermore, studies should aim to determine the growth performance, biomass production and metal accumulation of these species in metal contaminated soils for their better management and conservation.

Concerning *Taraxacum* (plants), data show that this species is tolerant to high metal concentrations, which supports the use as a bioindicator plant. Metals accumulated preferentially in roots, but also leaves proved accumulator organs, being able to store up to 200 mg kg^{-1} Pb and 160 mg kg^{-1} Zn, with only little damages (e.g. reduced foliar surface, reduced plant development).

Soil analysis of the studied area (data not reported) showed low pH, low cation exchange capacity, percentage of sand higher than 50 %, absence of structure and low capacity of the soil to retain water and metals. High heavy metal (Cd, Cr, Cu, Pb, Zn, Fe) concentrations were recorded in both soils and selected plants (*T. officinale*) growing on mine tailings. There is a relationship between metal content in soils and plants, which qualifies *T. officinale* as an indicator plant, rather than accumulator.

The ability of *T. officinale* to uptake and translocate heavy metals, particularly the essential micronutrients Zn and Fe, from soil to plant was ascertained.

Plants proved to accumulate heavy metals in their shoots more than in roots. This is an effective and cheap option for phytoremediation of contaminated areas and also to decrease erosion risk. The accumulation of metals in plants, however, affects the normal processes of plant metabolism. The study shows that there is a relationship between high metal contents in plants and their modified morphology: strong reduction of leaf thickness, modified parenchyma structure, and decreased mitochondria organization were ascertained, although toxic symptoms were apparently absent.

The evaluation of metal uptake by plants, combined with geobotanical observations, proved a useful tool to find tolerant plant populations to be used in revegetation programs aimed at reducing the environmental impact of contaminated areas. The selection of new genotypes from metal-tolerant species will bring large advances in phytoremediation of contaminated sites. Further investigations may help understanding if dandelion could be a metal-tolerant plant to grow on slightly metal-contaminated soils for restoration purposes (Maleci et al. 2013; Wahsha et al. 2011).

4.2 Case Study 2

4.2.1 Environmental Impact of PHEs on Native Flora Growing on Mine Dumps

Bioavailable heavy metals can enter the food chain through primary producers, reducing growth cycle and altering some biochemical pathways in plants (Loureiro et al. 2006). Moreover, heavy metals induce oxidative stress by generation of hydrogen peroxide, superoxide radical, hydroxyl radical and singlet oxygen, collectively termed reactive oxygen species (ROS) (Wahsha et al. 2012c; Verma and Dubey 2003). Many organic molecules are exposed to severe damage by free radicals after high accumulation of heavy metals in plants (Alfonso and Puppo 2009; Joshi et al. 2005). Formation of ROS in cells is associated with the development of many pathological states (e. g. reduced root elongation, seed germination, signaling imbalance) (Bini et al. 2008; Wahsha and Al-Jassabi 2009). This has contributed to the creation of the oxidative stress concept; in this view, ROS are unavoidable toxic products of O_2 metabolism, and aerobic organisms have evolved antioxidant defenses to protect against this toxicity (Alfonso and Puppo 2009). Oxidative stress can increase sharply in cells either due to the decrease in the activity of the antioxidant defense systems or to the overproduction of ROS (Wahsha et al. 2012d; Mukherjee et al. 2007; Soffler 2007). The most harmful effect induced by ROS in plants is the oxidative degradation of lipids, especially polyunsaturated fatty acids (PUFA) in cell membranes known as lipid peroxidation, which can directly cause biomembrane disorganization (Gobert et al. 2010; Wahsha et al. 2010; Timbrell 2009). Several studies reported that ROS can initiate lipid peroxidation through the action of hydroxyl radicals (Armstrong 2008; Katoch and Begum 2003). Lipid peroxidation reactions are usually free radical-driven chain reactions in which one radical can induce the oxidation of PUFA (Abuja and Albertini 2001). The lipid peroxide Malondialdehyde (MDA) is one of the major end-product of lipid peroxidation process (Yadav 2010). In this case, membrane destabilization and fusion are directly correlated with MDA production (Wahsha and Al-Jassabi 2009; Wahsha et al. 2010). The determination of MDA content is widely used as a reliable tool to detect the oxidative stress hazard by estimating the formation of lipid peroxides in biological material (Loureiro et al. 2006; Taulavuori et al. 2001; Zielinska et al. 2001). Furthermore, the formation of ROS and an increased MDA production were observed in plants exposed to different heavy metals as Cr, Pb, Cu and Zn under laboratory conditions (Aravind and Prasad 2003; Baryla et al. 2000; Sinha et al. 2005; Verma and Dubey 2003).

The LPO levels (expressed as MDA contents) in the common dandelion (*Taraxacum officinale* Weber ex F.H. Wigg. 1780), and different willows (*Salix purpurea* L.*, Salix caprea* L.*,* and *Salix elaeagnos* Scop.) vary proportionally with the level of heavy metals in soils of the corresponding site indicating a close relationship between MDA and metals, thus confirming the LPO test to be effective in environmental contamination assessment (see Table 5.6).

The control plants of *T. officinale* exhibited normal levels of LPO, and it was 0.2063 μM in leaves and 0.1450 μM in roots. There was a dramatic increase in MDA level in leaves and root homogenate from *T. officinale* collected from Imperina Valley. In agreement with previous results by Savinov et al. (2007), the increase of MDA production in *T. officinale* was expected because when heavy metal levels increase in soil their absorption by roots will increase, and the lipid peroxidation through the possible excessive generation of free radicals will be incremented. *T. officinale* responds to the increased heavy metal contents by intensification of LPO processes, which are related to the concentrations of Cu, Zn, Pb and Fe in the soil, as a result of an imbalance in the homeostasis of the antioxidant defence system (Alfonso and Puppo 2009).

Lipid peroxidation in leaves and roots of willows, measured as MDA content, are given in Table 5.6. Compared to control, heavy metals induced oxidative stress in willows was evident from the increased lipid peroxidation in roots, stems and leaves, indicating an enhanced MDA production, with MDA increasing in leaves in comparison to roots and stems. This is in agreement with data reported by Kuzovkina et al. (2004) and Ali et al. (2003). Generally, in both parts of the plant, the MDA contents were found to be positively correlated with metal accumulation ($p < 0.05$). The high level of MDA observed in investigated plants under metal stress might be attributed to the peroxidation of membrane lipids caused by ROS due to metal stress indicating a concentration-dependent free radical generation (Bini 2010; Ali et al. 2003).

Table 5.6 The contents of MDA of dandelion and willows

	MDA concentration (μM)	
Plant	Leaves	Roots
T. officinale	7.0	7.7
S. purpurea	34.4	28.8
S. eleagnos	32.9	25.3
S. caprea	29.6	24.9

The soils in the mining area are highly contaminated by trace elements, mainly Cu, Zn, Pb and Fe. The observed ability of *Salix* species and *T. officinale* to continue growth in the presence of heavy metals and to accumulate metals in their tissues, and particularly in leaves, demonstrated their tolerance to moderate to high levels of metals (has this already been states?). Therefore, they have good potential to be used in phytoremediation projects. Our results show that *T. officinale, S. purpurea, S. caprea* and *S. elaeagnos* exposed to great metal concentrations in soils result in an increment in LPO in their tissues, suggesting an important role of oxidative stress in the pathogenesis of heavy metal-induced cellular toxicity, and they can be a promising bioindicator for such research. The LPO process proved to be a useful tool for health assessment of wild-growing plant species, as it reflects the anthropic heavy metal pollution in ecosystems.

4.3 Case Study 3

4.3.1 Biological Soil Quality Evaluation of Mine Dumps

Heavy metals have been reported to disturb the ecosystem structure and functioning for long time, and the results of this study largely agree with published data (Wahsha et al. 2012a). Soil health is the continued capacity of the soil to function as a vital living system, providing essential ecosystem services. Within soils, all bio-geo-chemical processes of the different ecosystem components are combined. These processes are able to sustain biological productivity of soil, to maintain the quality of surrounding air and water environments, as well as to promote plant, animal, and human health (Karlen et al. 2001). A common criterion to evaluate long term sustainability of ecosystems is to assess the quality of soil. Recently, several bioindicators of soil quality and health have been reviewed (Chauvat et al. 2003; Parisi et al. 2005). Among them, microarthropods, due to their high sensitivity to respond to environmental changes, play a fundamental role in the dynamics of organic matter and in the fragmentation of soils, at different scales of time and space (Loranger-Merciris et al. 2007). Thus, they can also contribute to metal translocation through the ecosystem in polluted environments. The Soil Biological Quality index (QBS-ar), which is based on microarthropod groups present in the soil (Parisi et al. 2005), may be applied to assess its biological quality: the higher is the number of microarthropod groups adapted to soil habitats, the higher is soil quality.

In soil samples collected from abandoned mixed sulphide mine dumps of Imperina Valley, the QBS-ar values appeared to decrease significantly ($p < 0.05$) with respect to soil pollution by heavy metals. QBS-ar values appeared to decrease significantly ($p < 0.05$) with respect to soil pollution by heavy metals. The correlation matrix (R^2) between heavy metals in soil and QBS-ar values showed that QBS-ar values were negatively correlated with Fe (−0.102), Pb (−0.384), Cu (−0.405) and Zn (−0.702). Conversely, our QBS-ar values indicate a significant positive correlation with Cr (0.298) and Cd (0.55). The presence of Acarina, Symphyla, Protura and Collembola is important, being considered metal-tolerant (Migliorini et al. 2004): for example, Symphyla seem to be quite affected by high lead concentrations and our results show a decrease in their abundance in areas with high concentrations of Pb, Zn and Cu.

Former activities proved to affect the microarthropods community altering both quantity and quality of litter and the chemical-physical structure of the microhabitats. We found in the study area a moderate soil health status of the surface horizons due to the ecological success of secondary recolonization after abandonment, although affected by heavy metal contamination. Even if we could not find a statistical difference between QBS-ar and humus forms/ecosystem type, there seem to be different structures of microarthropods communities in terms of richness and evenness.

In this case we hypothesize that 50 years of biological restoration of the mine site could have improved the microarthropods biodiversity, driving humus development towards a better ecosystem functional stability. QBS-ar index proved a useful tool to evaluate soil biological health. However, there is an increasing need for further research focusing on soil health restoration assessment, combining QBS-ar index with soil bio-physical-chemical indicators.

5 Conclusion

It is imperative to acknowledge that current and future exploitation of mineral resources will produce even more wastes and impose more threats on Earth. Therefore, management and utilization of once unwanted mine wastes should be seriously considered through implementation of proper waste disposal management plans which focus on the utilization of wastes rather than considering it as unwanted.

References

Abuja P, Albertini R (2001) Methods for monitoring oxidative stress, lipid peroxidation and oxidation resistance of lipoproteins. Clin Chim Acta 306:1–17

Adriano DC, Chlopecka A, Kapland DI, Clijsters H, Vangrosvelt J (1995) Soil contamination and remediation. Philosophy, science and technology. In: Prost R (ed) Contaminated soils. £th ICOBTE, Colloques INRA Paris, 85, p 465–504

Alfonso DL, Puppo A (2009) Reactive oxygen species in plant signaling. In: Baluška F, Vivanco J (eds) Signaling and communication in plants. Springer, Heidelberg, pp 175–190

Ali MB, Vajpayee P, Tripathi RD, Ria UN, Singh SN, Singh SP (2003) Phytoremediation of lead, nickel, and copper by *Salix acmophylla* Boiss: role of antioxidant enzymes and antioxidant substances. Bull Environ Contam Toxicol 70:462–469

Alloway BJ (1995) Heavy metals in soils, IIth edn. Blackie Academic and Professional, Glasgow

Angelone M, Bini C (1992) Trace elements concentrations in soils and plants of Western Europe. In: Adriano DC (ed) Biogeochemistry of trace metals. Lewis Publishers, Boca Raton, pp 19–60

Aravind P, Prasad NV (2003) Zinc alleviates cadmium-induced oxidative stress in *Ceratophyllum demersum* L.: a free floating freshwater macrophyte. Plant Physiol Biochem 41:391–397

Armstrong D (2008) Advanced protocols in oxidative stress I. Humana Press, New Jersey, p 430

Baker AJM (1981) Accumulators and excluders strategies in the response of plants to heavy metals. J Plant Nutr 3:643–654

Baker AMJ, Brooks RR (1989) Terrestrial higher plants which hyperaccumulate metallic elements – a review of their distribution, ecology and phytochemistry. Biorecovery 1:81–126

Baker A, Mc Grath S, Reeves R, Smith J (2000) Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils. In: Terry N, Banuelos G (eds) Phytoremediation of contaminated soils. Lewis Publisher, London, pp 85–107

Bargagli R (1993) Plant leaves and lichens as biomonitors of naturals or anthropogenic emissions of mercury. In: Markert B (ed) Plants as biomonitors. WCH, Weinheim, pp 468–484

Baryla A, Laborde C, Montillet JL, Triantaphylides C, Chagvardieff P (2000) Evaluation of lipid peroxidation as a toxicity bioassay for plants exposed to copper. Environ Pollut 109:131–135

Bini C (2005) Plants growing on abandoned mine soils: a chance in phytoremediation. In: Proceedings of the III EGU conference, Wien (CD-rom)

Bini C (2007) From soil contamination to land restoration. I georgofili – quaderni 2007, 9. Società Editrice Fiorentina, Firenze, pp 41–62

Bini C (2010) From soil contamination to land restoration. In: Steinberg RV (ed) Contaminated soils: environmental impact, disposal and treatment. Nova Science Publisher, New York. ISBN 978-1-60741-791-0

Bini C (2012) Environmental impact of abandoned mine waste: a review. Nova Science Publishers, Hauppauge, New York, pp 92, ISBN 9781613248379

Bini C, Casaril S, Pavoni B (2000a) Fertility gain and heavy metal accumulation in plants and soils. Environ Toxicol Chem 77:131–142

Bini C, Maleci L, Gabbrielli L, Paolillo A (2000b) Biological perspectives in soil remediation with reference to chromium. In: Wise D (ed) Bioremediation of contaminated soils. Marcel Dekker, New York, pp 663–675

Bini C, Maleci L, Romanin A (2008) The chromium issues in soils of the leather tannery district in Italy. J Geochem Explor 96:194–202

Blaylock MJ, Elles MP, Nuttal CY, Zdimal KL, Lee CR (2003) Treatment of As contaminated soil and water using Pteris vittata. In: Proceedings of the VI ICOBTE, Uppsala, Sv

Brooks RR (1998) Phytochemistry of hyperaccumulator. In: Brooks R (ed) Plants that hyperaccumulate heavy metals: their role in phytoremediation, microbiology, archaeology, mineral exploration and phytomining. CAB International, Oxford, pp 15–53

Brooks RR, Robinson BH (1998) The potential use of hyperaccumulators and other plants for phytomining. In: Brooks R (ed) Plants that hyperaccumulate heavy metals: their role in phytoremediation, microbiology, archaeology, mineral exploration and phytomining. CAB International, Oxford, pp 327–356

Chauvat M, Zaitsev AS, Wolters V (2003) Successional changes of Collembola and soil microbiota during forest rotation. Oecologia 137:269–276

Chehregani A, Noori M, Yazdi HL (2009) Phytoremediation of heavy-metalpolluted soils: screening for new accumulator plants in Angouran mine (Iran) and evaluation of removal ability. Ecotoxicol Environ Saf 72:1349–1353

Chesworth W (2008) Encyclopedia of soil science, 1st edn. Springer Verlag, Dordrecht, pp 634–664

Corradi M, Bianchi A, Albasini A (1993) Chromium toxicity in Salvia sclarea. Effects of hexavalent chromium on seed germination and seedling development. Environ Exp Bot 33 (3):405–413

Dissegna M, Marchetti M, Vannicelli Casoni L (1997) I sistemi di terre nei paesaggi forestali del Veneto. Regione del Veneto, Dipartimento per le foreste e l'economia Montana

Ernst WHO (1993) Geobotanical and biogeochemical prospecting for heavy metal deposits in Europe and Africa. In: Markert B (ed) Plants as biomonitors. WCH, Weinheim, pp 107–126

Ernst WHO (1996) Bioavailability of heavy metals and decontamination of soils by plants. Appl Geochem 11:163–167

Fontana S, Wahsha M, Bini C (2010) Preliminary observations on heavy metal contamination in soils and plants of an abandoned mine in Imperina Valley (Italy). Agrochimica 54(4):218–231

Fontana S, Bini C, Wahsha M, Bullo M (2011) Heavy metals contamination in soils and their transfer to common wheat (*Triticum aestivum* L.): a case study. Geophys Res Abstr 13:1751–1

French CJ, Dickinson NM, Putwain PD (2006) Woody biomass phytoremediation of contaminated Brownfield land. Environ Pollut 141:387–395

Frizzo P, Ferrara E (1994) Mixed sulphides mine district of Agordo–Valsugana (Subalpine Basement, Eastern Alps). In: Proceedings of the special workshop in memory of Prof. Stefano Zucchetti, Torino, pp 147–154

Ghaderian SM, Mothadi A, Rahiminejad MR, Baker AJM (2007) Nickel and other metal uptake and accumulation by species of A*lyssum* (Brassicaceae) from the ultramafics of Iran. Environ Pollut 145:293–298

Giuliani C, Pellegrino F, Tirillini B, Maleci L (2008) Micromorphological and chemical characterization of *Stachys recta* subsp *serpentini* (Fiori) Arrigoni in comparison to *S. recta* sub sp. *recta* (Lamiaceae). Flora 203:376–385

Gobert M, Gruffat D, Habeanu M, Parafita E, Bauchart D, Durand D (2010) Plant extracts combined with vitamin E in PUFA-rich diets of cull cows protect processed beef against lipid oxidation. Meat Sci 85:676–683

Haque N, Peralta-Videa JR, Jones GL, Gill TE, Gardea-Torresdey JL (2008) Screening the phytoremediation potential of desert broom (*Baccharis sarothroides* Gray) growing on mine tailings in Arizona, USA. Environ Pollut 153:362–368

Helios-Rybicka E (1996) Impact of mining and metallurgical industries on the environment in Poland. Appl Geochem 11(1–2):3–11

Jabiol B, Brethes A, Ponge JF, Toutain F, Brun JJ (2007) L'humus sous toutes ses formes, 2nd edn. BIalec, Nancy, p 67

Jenny H (1989) The soil resource. Springer Verlag, New York, p 377

Jensen JK, Holm PE, Nejrup J, Larsen MB, Borggaard OK (2009) The potential of willow for remediation of heavy metal polluted calcareous urban soils. Environ Pollut 157:931–937

Jian-Min Z, Zhi D, Mei-Fang C, Cong-Qiang L (2007) Soil heavy metal pollution around the Dabaoshan Mine, Guangdong Province, China. Pedosphere 17(5):588–594

Joshi G, Sultana R, Tangpong J, Cole MP, Clair D, Vore M, Estus S, Butterfield DA (2005) Free radical mediated oxidative stress and toxic side effects in brain induced by the anti cancer drug adriamycin: insight into chemobrain. Free Radic Res 39(11):1147–1154

Jung MC (2001) Heavy metal contamination of soils and waters in and around the Imcheon Au–Ag mine, Korea. Appl Geochem 16:1369–1375

Jung MC, Thornton I (1996) Heavy metal contamination of soils and plants in the vicinity of a lead–zinc mine, Korea. Appl Geochem 11:53–59

Kabata-Pendias A (2004) Soil–plant transfer of trace elements – an environmental issue. Geoderma 122:143–149

Karlen DL, Andrews SS, Doran JW (2001) Soil quality: current concepts and applications. Adv Agron 74

Katoch B, Begum R (2003) Biochemical basis of the high resistance to oxidative stress in *Dictyostelium discoideum*. Indian Acad Sci 28(5):581–588

Keane B, Collier MH, Shann JR, Rogstad SH (2001) Metal content of dandelion (*Taraxacum officinale*) leaves in relation to soil contamination and airborne particulate matter. Sci Total Environ 281:63–78

Kidd P, Barcelo J, Bernal MP, Navari-Izzo F, Poschenrieder C, Shilev S, Clemente R, Monterroso C (2009) Trace element behaviour at the root–soil interface: implications in phytoremediation. Environ Exp Bot 67:243–259

Królak E (2003) Accumulation of Zn, Cu, Pb and Cd by dandelion (*Taraxacum officinale* Web.) in environments with various degrees of metallic contamination. Pol J Environ Stud 12(6): 713–721

Kuzovkina YA, Knee M, Quigley MF (2004) Cadmium and copper uptake and translocation of five *Salix* L. Species. Int J Phytoremediation 6(3):269–287

Lal R (2006) Encyclopedia of soil science, vol 2, 2nd edn. Taylor and Francis, New York, pp 275–443

Landberg T, Greger M (2002) Differences in oxidative stress in heavy metal resistant and sensitive clones of *Salix viminalis*. J Plant Physiol 159:69–75

Lee CG, Chon HT, Jung MC (2001) Heavy metal contamination in the vicinity of the Daduk Au–Ag–Pb–Zn mine in Korea. Appl Geochem 16:1377–1386

Lehoczky E, Szabados I, Marth P (1996) Cadmium content of plants as affected by soil cadmium concentrations. Commun Soil Sci Plant Anal 27:1765–1777

Lim HS, Lee JS, Chon HT, Sager M (2008) Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea. J Geochem Explor 96:223–230

Lopareva-Pohu A, Verdin A, Garçon G, Sahraoui AL, Pourrut B, Debiane D, Waterlot C, Laruelle F, Bidar G, Douay F, Shirali P (2011) Influence of fly ash aided phytostabilisation of Pb, Cd and Zn highly contaminated soils on *Lolium perenne* and *Trifolium repens* metal transfer and physiological stress. Environ Pollut 159:1721–1729

Loranger-Merciris G, Imbert D, Bernhard-Reversat F, Ponge JF, Lavelle P (2007) Soil fauna abundance and diversity in a secondary semi-evergreen forest in Guadeloupe (Lesser Antilles): influence of soil type and dominant tree species. Biol Fertil Soils 44:269–276

Lottermoser B (2010) Mine wastes characterization, treatment and environmental impacts, 3rd edn. Springer Verlag, New York, pp 1–40

Loureiro S, Santos C, Pinto G, Costa A, Monteiro M, Nogueira AJA, Soares A (2006) Toxicity assessment of two soils from Jales mine (Portugal) using plants: growth and biochemical parameters. Arch Environ Contam Toxicol 50:182–190

Malawska M, Wilkomirski B (2001) An analysis of soil and plant (*Taraxacum officinale*) contamination with heavy metals and polycyclic aromatic hydrocarbons (PAHs) in the area of the railway junction Ilawa Glòwna, Poland. Water Air Soil Pollut 127:339–349

Maleci L, Gentili L, Pinetti A, Bellesia F, Servettaz O (1999) Morphological and phytochemical characters of *Thymus striatus* Vahl growing in Italy. Plant Biosyst 133(2):137–144

Maleci L, Bini C, Paolillo A (2001) Chromium (III) uptake by *Calendula arvensis* L. and related phytotoxicity. In: Proceedings of the VI ICOBTE, Guelph, p 384 (abstract)

Maleci L, Buffa G, Wahsha M and Bini C (2013) Morphological changes induced by heavy metals in dandelion (Taraxacum officinale Web.) growing on mine soils. J Soils Sediments. doi:10.1007/s11368-013-0823-y

Mangabeira P, Almeida AA, Mielke M, Gomes FP, Mushrifah I, Escaig F, Laffray D, Severo MI, Oliveira AH. Galle P (2001) Ultrastructural investigations and electron probe X-ray microanalysis of chromium-treated plants. In: Proceedings of the VI ICOBTE, Guelph, p 555

Marchiol L, Sacco P, Assolari S, Zerbi G (2004) Reclamation of polluted soils: phytoremediation potential of crop-related *Brassica* species. Water Air Soil Pollut 158(1):345–356

Markert B, Breure T, Zechmeister HG (2003) Bioindicators an biomonitors – principles, concepts and applications. Elsevier, Amsterdam

Mc Grath S (1998) Phytoextraction for soil remediation. In: Brooks R (ed) Plants that hyperaccumulate heavy metals: their role in phytoremediation, microbiology, archaeology, mineral exploration and phytomining. CAB International, Oxford, pp 261–287

Meers E, Vandecasteele B, Ruttens A, Vangronsveld J, Tack FMG (2007) Potential of five willow species (*Salix* spp.) for phytoextraction of heavy metals. Environ Exp Bot 60:57–68

Migliorini M, Pigino G, Bianchi N, Bernini F, Leonzio C (2004) The effects of heavy metal contamination on the soil arthropod community of a shooting range. Environ Pollut 129(2): 331–340

Mleczek M, Lukaszewski M, Kaczmarek Z, Rissmann I, Golinski P (2009) Efficiency of selected heavy metals accumulation by *Salix viminalis* roots. Environ Exp Bot 65:48–53

Mukherjee PK, Ahamed KN, Kumar V, Mukherjee K, Houghton PJ (2007) Protective effect of biflavones from *Araucaria bidwillii* hook in rat cerebral ischemia/reperfusion induced oxidative stress. Behav Brain Res 178:221–228

Mun HW, Hoe AL, Koo LD (2008) Assessment of Pb uptake, translocation and immobilization in kenaf (*Hibiscus cannabinus* L.) for phytoremediation of sand tailings. J Environ Sci 20: 1341–1347

Navarro MC, Pérez-Sirvent C, Martínez-Sánchez MJ, Vidal J, Tovar PJ, Bech J (2008) Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. J Geochem Explor 96:183–193

Pandolfini T, Gremigni P, Gabbrielli R (1997) Biomonitoring of soil health by plants. In: Pankhurst C, Doube BM, Gupta VV (eds) Biological indicators of soil health. CAB Int, Wallingford, pp 325–347

Parisi V, Menta C, Gardi C, Jacomini C, Mozzanica E (2005) Microarthropod communities as a tool to assess soil quality and biodiversity: a new approach in Italy. Agric Ecosyst Environ 105: 323–333

Preeti P, Tripathi AK (2011) Effect of heavy metals on morphological and biochemical characteristics of *Albizia procera* (Roxb.) Benth. seedlings. Int J Environ Sci 1(5):1009

Pulford ID, Watson C (2003) Phytoremediation of heavy metal-contaminated land by trees – a review. Environ Int 29:529–540

Rosselli W, Rossi M, Sasu I (2006) Cd, Cu and Zn contents in the leaves of *Taraxacum officinale*. Swiss Federal Institute for Forest. Snow Landsc Res 80(3):361–366

Salt DE, Blaylock M, Kumar N, Dushenkov V, Ensley BD, Chet I, Raskin I (1995) Phytoremediation: a novel strategy for the removal of toxic metals from the environment using plants. Biotechnology 13:468–474

Sarret G, Vangronsveld J, Roux M, Coves J, Manceau A (2001) Bioaccumulation of metal in plants and microorganisms studied by electron microscopy and EXAFS spectroscopy. In: Proceedings of the VI ICOBTE, Guelph, p 555

Savinov AB, Kurganova LN, Shekunov YI (2007) Lipid peroxidation rates in *Taraxacum officinale* Wigg. and *Vicia cracca* L. from biotopes with different levels of soil pollution with heavy metals. Russian J Ecol 38(3):174–180

Selim HM, Sparks DL (2001) Heavy metals release in soils, 1st edn. Lewis Publishers, Boca Raton, pp 98–108

Simon L, Martin HW, Adriano DC (1996) Chicory (*Cichorium intybus* L.) and dandelion (*Taraxacum officinale* Web.) as phytoindicators of cadmium contamination. Water Air Soil Pollut 91(3–4):351–362

Sinha S, Saxena R, Singh S (2005) Chromium induced lipid peroxidation in the plants of *Pistia stratiotes* L.: role of antioxidants and antioxidant enzymes. Chemosphere 58:595–604

Soffler C (2007) Oxidative stress. Vet Clin North Am Equine Pract 23(1):135–157

Taulavuori E, Hellström E, Taulavuori K, Laine K (2001) Comparison of two methods used to analyse lipid peroxidation from *Vaccinium myrtillus* (L.) during snow removal, reacclimation and cold acclimation. J Exp Bot 52(365):2375–2380

Timbrell J (2009) Principles of biochemical toxicology, 4th edn. Informa Healthcare USA, Inc., New York

Turuga L, Albulescu M, Popovici H, Puscas A (2008) *Taraxacum officinale* in phytoremediation of contaminated soils by industrial activities. Ann West Univ Timisoara Ser Chem 17(2):39–44

Vandecasteele B, De Vos B, Tack F (2002) Cadmium and zinc uptake by volunteer willow species and elder rooting in polluted dredged sediment disposal sites. Sci Total Environ 299:191–205

Vasquez MD, Poschenrieder C, Barcelo J (1991) Ultrastructural effects and localization of low cadmium concentrations in bean roots. New Phytol 120:215–226

Vergnano Gambi O (1992) The distribution and ecology of the vegetation of ultramafic soils in Italy. In: Roberts BA, Proctor J (eds) The ecology of areas with serpentinized rocks. A world view. Kluwer Academic Press, Dordrecht, pp 217–247

Verma S, Dubey RS (2003) Lead toxicity induces lipid peroxidation and alters the activities of antioxidant enzymes in growing rice plants. Plant Sci 164:645–655

Wahsha M, Al-Jassabi S (2009) The role of Silymarin in the protection of mice liver damage against Microcystin-LR toxicity. Jordan J Biol Sci 2(2):63–68

Wahsha M, Al-Jassabi S, Azirun M, Abdul-Aziz K (2010) Biochemical screening of Hesperidin and Naringin against liver damage in Balb/c mice exposed to Microcystin- LR. Middle East J Sci Res 6(4):354–359

Wahsha M, Bini C, Fontana S, Zilioli D (2011) Phytotoxicity assay on soils and plants: elements for phytoremediation of mine soils. Geophy Res Abstr 13:1807–1

Wahsha M, Ferrarini A, Vannuzzo L, Bini C, Fontana S (2012a) Soil quality evaluation of Spolic Technosols. Case study from the abandoned mining site in Imperina Valley (Belluno, Italy). Environ Qual 9:1–9

Wahsha M, Bini C, Argese E, Minello F, Fontana S, Wahsheh H (2012b) Heavy metals accumulation in willows growing on Spolic Technosols from the abandoned Imperina Valley mine in Italy. J Geochem Explor 123:19–24

Wahsha M, Al-Omari A, Hassan M, Abuadas F, Ahmed E, Mostafavi K, Moradi M, Ghotbi M (2012c) Protective action of flavonoids extracted from different Jordanian plants against oxidative stress. Int J Biol Pharm Res 3(3):450–456

Wahsha M, Bini C, Fontana S, Wahsha A, Zilioli D (2012d) Toxicity assessment of contaminated soils from a mining area in Northeast Italy by using lipid peroxidation assay. J Geochem Explor 113:112–117

Wenzel WW, Sattler H, Jockwer F (1993) Metal hyperaccumulator plants: a survey on species to be potentially used for soil remediation. Agronomy Abstr p 52

Yadav SK (2010) Heavy metals toxicity in plants: an overview on the role of glutathione and phytochelatins in heavy metal stress tolerance of plants. South Afr J Bot 76(2):167–179

Yun-Guo L, Hui-Zhi Z, Guang-Ming Z, Bao-Rong H, Xin L (2006) Heavy metal accumulation in plants on Mn mine tailings. Pedosphere 16(1):131–136

Zhang XY, Lin FF, Mike TF, Wong XL, Feng XL, Wang K (2009) Identification of soil heavy metal sources from anthropogenic activities and pollution assessment of Fuyang County, China. Environ Monit Assess 154:1–4

Zielinska M, Kostrzewa A, Ignatowicz E, Budzianowski J (2001) The flavonoids, quercetin and isorhamnetin 3-O-acylglucosides diminish neutrophil oxidative metabolism and lipid peroxidation. Acta Biochim Pol 48(1):183–189

Zupan M, Hudnik V, Lobnik F, Kadunc V (1995) Accumulation of Pb, Cd, Zn from contaminated soil to various plants and evaluation of soil remediation with indicator plant (*Plantago lanceolata*). In: Prost R (ed) Contaminated soils. INRA, Paris, pp 325–335

Zupan M, Kralj T, Grcman H, Hudnik V, Lobnik F (2003) The accumulation of Cd, Zn, Pb in *Taraxacum officinale* and *Plantago lanceolata* from contaminated soils. In: Proceedings of the VII ICOBTE, Uppsala Sv