# Phytoremediation and Environmental Factors

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## 4.1 Introduction

Phytoremediation includes a range of plant-based remediation processes such as phytoextraction, phytostabilization, phytoimmobilization, rhizofiltration, and phytovolatilization (Alkorta et al. 2004; Ali et al. 2013; Vithanage et al. 2012). Among all of these techniques, phytoextraction is crucial, because the principle of this technique is metal translocation to shoots and bioconcentration is observed in the above ground parts of the plant species (Peuke and Rennenberg 2005; Vithanage et al. 2012). This is all the more important when the harvest of root biomass is generally not feasible (Zacchini et al. 2009; Tangahu et al. 2011; Ali et al. 2013). However, the efficiency of phytoextraction (as well as other techniques of phytoremediation) depends on numerous coupled environmental factors. Generally, they can be defined as factors influencing the lives of organisms and which are essential to their correct functioning in land and water environments. The most universal division of environmental factors distinguishes two main groups, namely, biotic (living) and abiotic (nonliving) factors (Schulze et al. 2005). The biotic group includes plants, animals, protists, fungi, and bacteria, whereas the abiotic group includes weather (rain, insolation, temperature, cloud, snow), pH, rocks, oceans, and rivers, as well as anthropogenic factors (all the factors that are products of human activity, e.g., organic and/or inorganic pollutants). The characteristic traits of all mentioned factors are in mutual interrelation; therefore, when one factor is changed, the whole system can be altered (Atwell et al. 1999; Beard et al. 2005). However, the phytoextraction potential depends on external environmental factors, but also on internal plant factors. Interest in phytoextraction has grown due to the identification of metal

phytoaccumulator plant species (Seth 2012) and their high capacity for adaption to environmental conditions. Plants are able to adapt to disadvantageous environmental conditions (growth in significantly polluted areas, drought, salinity), and two main strategies are used: stress avoidance and tolerance. Selection of plants used in phytoremediation is extremely important and has been presented in numerous scientific works, both in hyperaccumulator and non-hyperaccumulator plants (Hendriks et al. 2003; Mleczek et al. 2010). The mentioned plants produce numerous chemical compounds able to stimulate or inhibit plant growth especially in unfavorable environmental conditions (Davies 1987; Dimkpa et al. 2009). The growth-promoting substances include phytohormones, bioregulators, and biostimulators, where, e.g., auxins (Chalupa 1984; Dimkpa et al. 2008; Liphadzi et al. 2010), cytokinins (Ei-D et al. 1979; Cassina et al. 2011), and gibberellins (Pandey et al. 2007) are stimulators, and abscisic acid is an inhibitor (Park et al. 2009). Also, plants activate a defense mechanism combined with the exudation of specific molecules into the environment and adaptive changes in plant structure and growth to withstand the adverse growth conditions (Drzewiecka et al. 2012). These specific molecules include:

- (i) Metal-binding peptides created from glutathione (GSH)—phytochelatins (PCs) (Grill et al. 1987; Rauser 1995)
- (ii) Low molecular weight, metal-binding proteins metallothioneins (MTs) (Cobbett and Goldsbrough 2002; Kägi 1993)
- (iii) Amino acids with especially the role of histidine (Leszczyszyn et al. 2007)
- (iv) Phytin (Rauser 1999)
- (v) Low molecular weight organic acids (LMWOAs) secreted into the rhizosphere (Magdziak et al. 2011; Li et al. 2012a, b)
- (vi) LMWOAs produced in plant tissue (Adeniji et al. 2010)
- (vii) Flavonoids (Ebrahimzadeh et al. 2008; Fernandez et al. 2002)

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The amount and the kind of molecules occurring in a given plant together with specific traits of certain plant taxa determine the ease of plants' adaptation to new environmental conditions, biomass crop, and at the same time efficiency of trace element accumulation. In this regard, plant selection has fundamental importance in phytoextraction efficiency, but the influence of external factors although variable (interaction between elements in polluted soil) is also permanent (abiotic factors). For this reason, it is not possible to determine the precise efficiency of trace element accumulation. The range of tolerance together with maximum, optimum, and minimum of particular factor values decides about the plant tolerance as well as plant ability to adapt to these factors (Chapin et al. 1987; Atwell et al. 1999). Due to the size constraints on this chapter, the characterization of all environmental factors is impossible. Therefore we present only some of them, which are most frequently analyzed or commented on in scientific environmental studies.

## 4.2 Environmental Factors

Proper plant growth is not possible without adequate amounts of water fulfilling the primary role in normal plant functioning. Due to the difference in water potential  $\Psi$  in the soil, plant, and atmosphere, the natural flow of water from the soil to the atmosphere occurs. The presence of conditions for the occurrence of the phenomenon determines the transport of numerous substances and compounds playing an important role in the life processes of plants (Tien et al. 1979; Chen and Aviad 1990). Therefore, this seemingly small polar molecule with a high thermal capacity allows the elongation growth of cells and tissues of plants. The amount of available water affects the physiological and biochemical processes of plants (Hanson and Hitz 1982; Al-Karaki and Al-Raddad 1997; Maggio et al. 2000; Asrar and Elhindi 2011). For the proper functioning of the individual cell structures, it is important to maintain a sustainable water balance, because changes in water availability result in altering growth, yield, and water relations (Abdel-Fattah et al. 2002; Wu and Xia 2006; Ibrahim et al. 2011) and metabolic pathways (Subramanian and Charest 1995; Asrar and Elhindi 2011; Asrar et al. 2012). However, the root system plays the essential role in providing water, nutrients, and physical support to the plants. It is the major plant organ, which receives most stress factors and as a response to environmental factors starts the modulation of organs and then tissue in response to changing conditions of the external environment (Kummerová et al. 2013). In the event of water deficiency, the plant growth is significantly reduced due to osmotic stress resulting from decreasing soil water potential and uptake of nutrients (Auge 2001; Lee et al. 2007; Seagraves et al. 2011) and increased levels of nitrogenous compounds in plants due to increased protein hydrolysis, and the accumulation of osmoprotectants is observed

(Seagraves et al. 2011). Moreover, the changes in root physiology and morphology depend on the level of groundwater (Zencich et al. 2002), providing an additional and important water source, and with it the minerals, which next to rainfall, are considered to be the main source of water for plants (Ehleringer and Dawson 1992). In the case of water stress in the upper soil layer, it leads to increased root length and reduced diameter, which reduces the resistance of roots to water uptake, so crop roots actively absorb water from the subsoil (Costa et al. 2000; Hendrick and Pregitzer 1996; Li et al. 2012a, b), while in the case of water excess, formation of anaerobic conditions in the root zone area is observed. Associated with this is the reduction of selective permeability of plant roots, which then is connected with accumulation of both essential and toxic elements. This situation is especially seen in the case of plants with a small annual growth increase in flooded areas (even more than half the height of plants) and where an increase in water level occurs for a long time, resulting in wilting of most of them (Dinicola 2006). Metals such as Zn, Ni, and Cd in water-logged soils are less available, because of decreased solubility resulting in low redox potential and formation of sparingly soluble sulfides (Rieuwerts et al. 1998; Hammer and Keller 2002). The most important hyperaccumulators of different metals (Ni, Co, Zn) originated from areas with dry, hot summers and/or grow on skeletal soil with very low water holding capacity (Reeves and Brooks 1983). For hyperaccumulator plants metal bioavailability is an important factor affecting uptake. High soil moisture usually does not negatively affect growth and metal accumulation by hyperaccumulators. Angle et al. (2003) confirmed that high soil moisture stimulated growth and metal uptake by hyperaccumulators of Ni such as Alyssum murale and Berkheya coddii and of Zn such as Thlaspi caerulescens, which generally grow on low moisture soil. On the other hand, low moisture enhanced Se accumulation and reduced biomass production of Festuca arundinacea (Tennant and Wu 2000).

But, with access to water, it involves not only the structure of the root system and further plant development but also the availability of plant nutrients (essential and toxic elements). Different water content and different chemical and biological properties of soil/roots from the rhizosphere zone and from bulk soil can affect nutrient bioavailability to the plant. It is evident that bioavailability of metals could be artificially increased under optimum or a little above water resources. Water is the main source of macronutrients (K, N, P, S, Ca, and Mg) but also micronutrients (Fe, Zn, Cu, Ni, and Mo) and toxic elements (Pb, Cd, and Hg). Their presence is an important contribution to the life processes of plants and their growth. Their amount in water, as an important medium, is not decisive, because plants developed a selective mechanism to acquire some element ions in spite of others, and selective absorption of elements depends on the membrane transporter properties (Salt et al. 1995; Seth 2012). By these specific transporters are able to recognize, bind, and then mediate the transmembrane transport of ions. However,

under metal-polluted soil, plants take up not only essential nutrients but also significant amounts of toxic elements, such as Cd, Hg, and Pb. Essential nutrients and toxic trace elements are absorbed by the same processes, so under increased concentrations of nonessential elements, plants are not able to distinguish between the two ions. Therefore, at high levels of toxic metals, there follows competition between ions, and the plant starts to retrieve the component that dominates in the environment. Moreover, in the case of plants, accumulation of all contents begins, as mentioned above, at the roots, which are a crucial element affecting the efficiency of phytoextraction. The most important is the mobility of elements in the soil and their availability to the cells of the roots, which may result in further transport of metal-containing sap to aboveground parts of the plant. It should be noted that the transfer process is controlled by two factors: the root pressure and transpiration of leaves, which are contingent on water resources in the soil environment (Seth 2012). Stress associated with water availability leads to disruption of water potential gradients, loss of turgor, disruption of membrane integrity, and denaturation of proteins.

Soil is the most important environmental factor in the growth and development of plant life. However, it must be mentioned that soil has indeed a diverse composition, with no regular and predictable structure, as a result of which part of soil may have significantly different physical, chemical, and biological properties from another part located in close proximity. It all depends on many factors, including composition of mineral and organic matter, soil water, aeration, climate, the presence of soil bacteria and fungi, and animals inhibiting the ground. All of these parameters have essential effects on plant life, but also are an important issue in effectiveness of the phytoremediation process. Dynamic changes that occur in the soil environment not only determine development or inhibition of plant growth but also have a significant impact on the remediation process. However, among the numerous abovementioned parameters which determine the process of phytoremediation in soil, the most significant impact is the type of pollution (Wang 1994; Gonzales et al. 2013), because soil may be polluted by natural aromatic and hydrocarbon compounds and man-made chemicals (pesticides, herbicides, fungicides, and antibiotics) and metals. In the case of organic pollutants, their metabolism generally results in degradation into nontoxic substances that can be used by the plants and their microbial partners as a source of carbon, phosphorous, nitrogen, sulfur, and, in the some cases, trace elements (Saier and Trevors 2010). In the case of metals, the situation is much more complicated. Metals are not readily removed or degraded by chemical or microbial processes and in consequence are accumulated in soils and aquatic sediment (Ojegba and Fasidi 2007). This problem can be solved through the use of plants with increased tolerance to metals and the phytoremediation process. During the phytoremediation process, plants may transport trace elements in their cell walls, chelate them in the soil in inactive forms using secreted organic com-

pounds, or complex them in their tissue after transporting them into specialized cells and cell compartments. Metals may be stored in vacuoles safe from the sensitive cytoplasm where most metabolic processes occur. Plants also make chelating peptides such as cysteine and small proteins such us phytochelatins and metallothioneins that are stored safely in vacuoles (Saier and Trevors 2010). However, the effectiveness of phytoremediation depends mainly on the bioavailability of trace elements in soil, and their bioavailability strictly depends on soil solution properties (Chen et al. 2006). Chemical properties of soil-such as pH, Eh, and nutrient content-influenced the metal forms present in the soil and their accumulation (de la Fuente et al. 2008). However, it is important that a large proportion of metals in soil is immobilized, because they are bound with selected matrix components (Sheoran et al. 2011; Ali et al. 2013; de la Fuente et al. 2008), and only a fraction of soil metal is bioavailable for uptake by plants (Lasat 2002). For this reason the cleanup of soils contaminated with heavy metals (HMs) is one of the most difficult tasks for environmental engineering (Li et al. 2013). However, before plants are able to absorb and then accumulate metals, there must be a process involving activation of metals in the environment; in other words, there must be a process in which metals will be bioavailable to the plants.

Transport of heavy metals in the soil depends to a large extent on the chemical form of the metal. In the initial phase of the metal-soil contact, metal reactions are fast (minutes, hours). For this reason, natural consequences are various chemical forms of the metals and their different bioavailability, mobility, and toxicity (Shiowatana et al. 2001; Buekers 2007). The distribution of the metals in the soil is conditioned by factors such as precipitation or dissolution reactions, ion exchange, adsorption and desorption, immobilization of the biological activation, and plant species (Levy et al. 1992). Nevertheless, having an influence on all these parameters is the pH value, which is one of the parameters determining the metal speciation in soil. The trace elements that commonly occur as impurities in soil and for which the pH value is an important factor in the form of their occurrence include lead (Pb), chrome (Cr), arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni).

How does the pH affect the metals' occurrence in soil?

#### Pb

The lead phosphates, carbonates, (hydr)oxides, and sulfide are the dominant Pb compounds presented in the soil environment (Raskin and Ensley 2000). Their properties change depending on pH value, and insoluble forms occur when the pH is above 6 (Raskin and Ensley 2000). In conclusion, the mobility of Pb increases with decreasing pH value.

#### Cr

Chromium commonly found in contaminated areas can occur in the  $Cr^{3+}$  or  $Cr^{6+}$  oxidation state, depending on the pH and redox

conditions of the soil.  $Cr^{6+}$  is the dominant form where aerobic conditions exist, whereas in the presence of organic matter,  $S^{2-}$ or Fe<sup>2+</sup> ions under anaerobic conditions can be reduced to  $Cr^{3+}$ . It is also important to note that  $Cr^{6+}$  is the more toxic form and moreover more mobile with increasing pH. Chromium mobility decreases with the decrease in the oxidation state degree due to the increasing adsorption reaction to clays and oxide minerals below pH 5, and low solubility above pH 5, due to the hydroxide  $Cr^{3+}$  (III) formed in the solid form (Chrostowski et al. 1991). On the other hand, the Cr mobility is relevant to physicochemical properties of the soil, which determine the sorption properties due to the content of clay, iron oxide, and also the amount of organic matter.

### As

The toxicity of As is determined by the form in which it occurs (depending on whether it is in the As<sup>3+</sup> or As<sup>5+</sup> form or as organic). The As speciation highly determines its toxicity and bioavailability as well as determining the establishment of an adequate transport mechanism (Larios et al. 2012; Larsen et al. 1998). It is known that inorganic forms are more toxic and mobile than organoarsenic forms. Among inorganic forms of As, it was found that arsenite (As<sup>3+</sup>) is 10 times more toxic and mobile than arsenate (As<sup>5+</sup>) (Demirbas 2001; Lasota et al. 1968, 1980) and 70 times more than monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) (Demirbas 2001; Le et al. 1994; Londesborough et al. 1999; Niedzielski et al. 2013). However, the bioavailability of As is determined by the pH, and As mobility increases with increasing pH value (Smith et al. 1995).

## Cd

Cadmium may be present in the soil as a result of application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge). The disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and the bioavailability of this Cd determines whether plant Cd uptake occurs to a significant degree (Weggler et al. 2004). But it should be underlined that Cd mobility strictly depends on pH value, and the acidification of soils increases the geochemical mobility of Cd (Campbell 2006). In the case of Cd, the bioavailability to plants (as well as other organisms such as animals or humans) is important because once absorbed by an organism, it remains resident for many years (Wuana and Okieimen 2011).

## Cu

Copper is an element that forms stable complex compounds with organic material; therefore, only a small part of Cu ions or in more bioavailable organic forms are present in soil solution. The pH value is strictly associated with Cu solubility in the environment (solution), which significantly increases at pH 5.5 (Martínez and Motto 2000), which is rather close to the ideal farmland pH of 6.0–6.5 (Eriksson et al. 1997).

## Hg

In the soil environment mercury may exist in mercuric (Hg<sup>2+</sup>), mercurous (Hg<sub>2</sub><sup>2+</sup>), elemental (Hg<sub>0</sub>), or alkylated form (methyl/ ethyl mercury), but pH is a factor which determines the form in which Hg will be present. Moreover, sorption to soils, sediments, and humic materials is an important mechanism for the removal of Hg from solution. Sorption is a pH-dependent process and increases as pH increases. In consequence, the amount of bioavailable forms of mercury increases with the pH decrease of the environmental (Wuana and Okieimen 2011).

### Ni

In the case of Ni speciation under neutral pH or slightly alkaline soil environment, the hydroxide of Ni, which is a stable compound, is precipitated. The precipitate is readily soluble in acid solutions, consequently giving compounds of Ni<sup>3+</sup>, while under strongly alkaline conditions, a soluble form of nickelite ion (NO<sub>2</sub><sup>-</sup>) is formed. However, it should be noted that in the case of the soil, the greater part of all the Ni compounds that are released into the environment are adsorbed on soil particles, which become immobile as a result. In the case of Ni, the mobility significantly increases in acidic soils, making it more bioavailable, and often leaches down to the adjacent groundwater (Wuana and Okieimen 2011).

In the soil solution, siderophores have a significant impact; they are small molecule chelating compounds with high affinity to Fe<sup>3+</sup> ions and having the ability to bind trace elements (Al, Cd, Cu, Ga, In, Pb, Zn) and are produced by plants, bacteria, and fungi (Kidd et al. 2009; Rabeda et al. 2011). In the case of plants, the metal-mobilizing compounds secreted by roots into the rhizosphere are called phytosiderophores (Lone et al. 2008), which have certain mechanisms for solubilizing heavy metals in soil. Generally, only a fraction of soil metals are bioavailable for uptake by plants (Lasat 2002). In addition, plants growing in areas contaminated by high amounts of trace elements are characterized by a low content of iron in plant tissue. This generally results in chlorosis associated with iron deficiency, which is the consequence of the inhibition of chloroplast development and chlorophyll biosynthesis (Imsande 1998). The presence of bacteria in the rhizosphere, with the simultaneous presence of iron-siderophore complexes, is an additional source of iron for plants in polluted conditions (Bar-Ness et al. 1991; Reid et al. 1986; Wang et al. 1993). Strong binding of heavy metals to soil particles or precipitation makes a significant fraction of soil heavy metals insoluble and therefore mainly unavailable for uptake by plants (Sheoran et al. 2011). Due to secretion of H<sup>+</sup> ions by roots, the rhizosphere is acidified, and in consequence metal dissolution increases. The presence of H<sup>+</sup> ions allows displacement of heavy metal cations adsorbed to soil particles (Alford et al. 2010) and, in most cases, lower soil pH, promoting desorption of metals and increase of their concentration in solution (Thangavel and Subbhuraam 2004).

Furthermore, the rhizospheric microorganisms (mainly bacteria and mycorrhizal fungi) may significantly increase the bioavailability of heavy metals in soil (Vamerali et al. 2010; Sheoran et al. 2011). Interactions of microbial siderophores can increase labile metal pools and uptake by roots (Mench and Bes 2009; Ali et al. 2013). Bacteria are an important factor of soil, because they have the ability to mineralize organic matter, improving bioavailability and effectiveness of nutrient uptake (Domínguez-Crespo et al. 2012). Bacteria present in soil have a significant impact on phytoremediation, especially those bacteria which belong to the plant growth-promoting rhizobacteria/bacteria (PGPR/ PGPB) group. Also, the presence of PGPR bacteria is very important in areas contaminated with heavy metals, as it is conducive to the process of plant growth, inhibits the development of chlorosis, and increases the resistance of plants to increased metal content in the soil environment (inter alia abovementioned Ni, Pb, or Cu). Bacteria in the rhizosphere are involved in the accumulation of trace elements potentially toxic to plant organs (Jing et al. 2007). What is more, at the same time, the presence of bacteria affects the reduction of phytotoxicity of contaminated soil. This is due to the fact that the plant-bacterium together forms a specific arrangement in which the plant provides the bacteria the organic carbon (e.g., by molecules/compounds secreted by the cells of the root), which in turn induces the bacteria to reduce the phytotoxicity of the soil. In addition, bacteria and plants are in a symbiotic relationship by which microbial activity results in degradation of contaminations. Moreover, the components secreted into the root zone by the plant roots increase metal bioavailability and consequently increase the possibility of further phytoremediation abilities of bacteria. This mechanism increases the ability of plants to adapt to unfavorable conditions in the presence of metals, as well as increasing the phytoremediation potential by the presence of plant-bacterium symbiosis (Jing et al. 2007). Moreover, bacteria in the soil are usually present in large amounts, have a high surface area and metabolic activity, affect the bioavailability and toxicity of heavy metals by adsorption and dissolution, and carry out oxidation-reduction reactions or association of bacteria with organic and inorganic colloids (Shen and Yang 2008). The presence of bacteria in the root zone may have a beneficial effect because they are able to produce a series of compounds, which may be used by plants, and their presence leads to increased plant ability to absorb nutrients contained in the medium and also changed morphology of the roots (increased spreading), thus increasing the collection surface area (Rabeda et al. 2011). These mechanisms occurring in the soil in the presence of bacteria, presented, for example, in Brassica juncea growing on soil contaminated by Cd, Cu, P, or bound Zn with simultaneous presence of Azotobacter chroococcum or Bacillus megaterium, leading to lower toxicity, and even neutralization of toxic elements with respect to the plants, as a consequence result in increased efficiency of the phytoremediation process. This is due to the fact that on the surface of the cell walls of bacteria are present sulfhydryls and carboxyl groups and also a number of specialized proteins embedded in the cell wall and cell membrane, which limit the toxicity of the metal. Furthermore, microbes will produce metal-resistant genes composed of structural genes and regulatory genes to reduce the toxicity of heavy metals through many approaches. However, it should be noted that the siderophores produced by gram-positive and gram-negative bacteria are the most effective agents in metal complexing in the soil solution. In conclusion, the ability of activating metal absorbed onto the soil fraction, followed by complexation and their accumulation in the phytoremediation process, significantly depends on bacteria present in the soil environment.

An important factor in trace element availability in the soil environment, next to bacteria, is the effect of fungi, due to the fact that they are closely involved in the carbon cycle in nature. Through the ability to decompose organic matter, they take a significant role in the distribution of generated energy, and also conversion of proteins from plant residues on the nitrogen dissolved in the acidic form or NH<sub>4</sub><sup>+</sup> ions, which are more easily available forms for plants. In addition, mushrooms are involved in the circuit of inorganic components (Domínguez-Crespo et al. 2012). Also through the presence of plant-fungus symbiosis, the plant becomes much more resistant to environmental stress (Khan 2005; Gamalero et al. 2009; Rabęda et al. 2011). The presence of mycorrhizal fungi on the one hand can significantly increase the absorbent surface area of the root system and consequently allows better nutrition of the plants and on the other hand results in significantly increased accumulation of metals in the cells (Liang et al. 2009; Rabeda et al. 2011).

Moreover, the mycorrhizal fungi—as outlined above for bacteria—may produce siderophores, but also may secrete other components whose presence has a significant impact on the physical and chemical properties of the soil environment, which in turn contributes to the activation or inhibition of the processes taking place in soil. One of them is glomalin (Gonzalez-Chavez et al. 2004), whose presence in the soil is strongly associated with trace metals present in soil. Also, like plants, fungi secrete into the rhizosphere other molecules, such as organic acids, enabling the activation of the substrate metal, complexion, detoxification, and increased efficiency of accumulation (Magdziak et al. 2012; Vaněk et al. 2012).

It is worth emphasizing the presence of salts in the soil solution, which in addition to water is another important factor significantly influencing the growth of plants, as well as modifying the efficiency of accumulation of trace elements from the environment (Atkinson et al. 2007). The increasing salinity of soil occurring all over the world reduces growth of plants mainly by water deficit in the root zone, causing a number of changes in the homeostasis of cells at the molecular, physiological, and biochemical level. Salinity is a stress factor influencing plants, which is connected mainly with the negative effect of Na+ toxicity for cell metabolism and oxidative damage of plants related to formation of reactive oxygen species (ROS) (Manousaki and Kalogerakis 2009). It also affects the metabolism of soil organisms, leading to a major reduction of soil fertility. Salinity has toxic and/or osmotic effects affecting the use of hyperaccumulators to decontaminate polluted soil. Because salinity can change the bioavailability of metals in soil, salinity is a key factor in translocation of the metals from roots to aerial parts of the plant (Otte 1990; Fitzgerald et al. 2003; Manousaki et al. 2008). The authors suggested that metal accumulation in saline conditions can be very useful in enhancing phytoremediation processes. Manousaki and Kalogerakis (2009) revealed that cadmium uptake by cadmium and lead-tolerant Atriplex halimus L. increased with increasing salinity, because of higher bioavailability of the metal in soil. They suggested that it was achieved by displacement of cadmium from binding sites in soil matrix by Na<sup>+</sup>, solubilization of organic matter bound with the metals, or formation of soluble chloro-complexes of Cd which tend to shift Cd from the solid phase (Norvell et al. 2000; Weggler et al. 2004; Wahla and Kirkham 2008). Salinity of storm water could change metal uptake through the toxic effect of Na<sup>+</sup> and Cl<sup>-</sup> (Fritioff et al. 2005). Because Na<sup>+</sup> can release Cd from the sediment to the water, it causes an increase of cadmium concentration in water (Greger et al. 1995). Increasing salinity reduced metal accumulation (Cu, Zn, Cd, Pb) in submersed plants Elodea canadensis and Potamogeton natans L. (Fritioff et al. 2005). The Ni accumulator Alvssum murale was documented to be highly salt resistant in terms of seedling emergence and survival of emerged seedlings, while the Zn accumulator Thlaspi caerulescens was salt sensitive in low concentrations of Ni and Zn. High concentrations of the metals did not have a clear effect on salt tolerance (Comino et al. 2005). The experiment was carried out with NaCl concentration of 0.25, 50, and 100 mM. Another experiment indicated that in some plant non-hyperaccumulators of any metal, such as Tamarix ramosissima, the Cd uptake significantly increased with elevating salinity. Additionally, the salinity affected the translocation of Cd from roots to the aerial parts of plants, and no visible signs of metal toxicity were observed (Manousaki et al. 2008). Because of Cd tolerance and high production of biomass, the authors suggested the use of T. ramosissima for phytoremediation of cadmium-contaminated soil.

It should also be noted that the growth of plants significantly depends on the air temperature, implying the widely discussed nowadays global warming. Global warming is associated with increased concentration of carbon dioxide  $(CO_2)$  and other greenhouse gases in the atmosphere by natural and anthropogenic activities (Cox et al. 2000; Qaderi

and Reid 2009; Oaderi et al. 2012). Industrialization dramatically changes the biological, chemical, and physical properties of the environment via the increase of atmospheric CO<sub>2</sub> concentration despite reduction of CO<sub>2</sub> emissions. A positive effect of elevated atmospheric CO<sub>2</sub> concentration on heavy metal phytoextraction in polluted soil was documented, e.g., Pinus densiflora and Pteridium revolutum, via increasing production of biomass or uptake of heavy metals from soil (Jia et al. 2010; Kim and Kang 2011; Zheng et al. 2008). What is more, higher  $CO_2$  concentration will result in an overall increase of the surface air temperature in the coming decade, extrapolating from the existing records (Smith et al. 2007; Qaderi et al. 2012), which also may lead to enhanced plant metabolism and increased development (Larcher 2003; Qaderi and Reid 2009). The responses to higher temperatures depend on plant developmental stage and the character of temperature increase. Observed higher temperature, under global warming, stimulates plant growth, photosynthetic capacity, and decomposition of soil organic matter, which affects mobilization of metals. The bioavailability of elements such as Ag, Cu, Zn, Fe, Sb, and Cu increased, which consequently resulted in an increase of phytoextraction efficiency (Baghour et al. 2001: Li et al. 2012a, b: van Gestel 2008). Temperature also had a positive effect on Cu, Zn, and Cd uptake by submersed plants Elodea canadensis and Potamogeton natans L. (and also for Pb), and high temperature together with low salinity led to nearly twofold elevated metal concentration in comparison to low temperature or high salinity (Fritioff et al. 2005). However, apart from the positive effects of higher temperatures in phytoextraction, one should pay attention to the negative side of warming. It has been predicted that global warming will cause more frequent and prolonged drought periods. Limited water supply can affect tree species and lead to dieback of sensitive species. Drought led to stomata closure and restriction of CO<sub>2</sub> input, which causes imbalances between excitation energy driving electron transport and electron consumption in Calvin cycle reactions (Flexas et al. 2004; Tausz et al. 2004). These imbalances cause the formation of harmful reactive oxygen species (ROS) and (photo-)oxidative stress (Tausz et al. 2004). Antioxidative and photoprotective defense systems counteract damage caused by ROS (Smirnoff 1993). Reactive oxygen species also results in photosynthesis decrease, but increased transpiration and stomatal conductance, and in turn, reduced plant biomass (Jones 1992; Nobel 2009; Qaderi and Reid 2009), due to the fact that plants usually produce smaller leaves and extensive root systems to increase water uptake from soil but reduce water loss from leaves (Gliessman 1998).

It is worth underlining that a significant role in soil is also played by animals inhabiting the soil environment. While the composition of organic matter is conditioned by many factors, as described above, a little should be mentioned about the animals inhabiting the soil environment, in particular earthworms. They are an essential part of the soil fauna and are regarded as a useful indicator of soil health and quality. The most important role of earthworms in soil is organic matter decomposition and subsequent cycling of nutrients. Also, data available in the literature indicate that their presence in the soil may have humifying action, because some humic acids are detected only in soil where earthworms are present (Spurgeon et al. 2003; Sizmur and Hodson 2009). For this reason they have a biological impact on soil pollutants, because it is known that organic metal compounds are more bioavailable due to the fact that microorganisms inhabiting the soil while the metals are released in solution readily decompose organic components. Next, metals consequently released into solution may be chelated by compounds produced by earthworms and further absorbed and taken up by the plants (Ruiz et al. 2011). Moreover, earthworms have a direct impact on the cycle and metabolism of nutrients, which has a significant impact on the physical, chemical, and biological properties of the soil. Sizmur and Hodson (2009) presented a conceptual model of how earthworms may impact metal chemistry in soil, and regardless of the type of soil, the results clearly show that the presence of earthworms affects the bioavailability of elements. Physical and chemical properties of the soil have a significant impact on the phytoextraction process, indicated by the fact that numerous studies on remediation of soils in contaminated areas have shown how by modifying the properties of the soil one can increase the accumulation process and at the same time accelerate the remediation process. For this reason, the development of phytoremediation as a useful technique for soil remediation is focused on soil properties, where metals occur in soluble form, easily accumulated by plants (Lasat 2002).

# 4.3 Conclusions

- Phytoremediation is the complex of environment purity improvement techniques based on plants' abilities and depends on several environmental factors.
- Oxidative stress associated with water availability influences the techniques' efficiency.
- Soil is the most important environmental factor in the effectiveness of the phytoremediation process.
- Availability for plants of trace elements contaminating the environment depends on pH value of the soil and/or water.
- Rhizospheric microorganisms may significantly increase the bioavailability of trace metals.
- Salinity of soil reduces growth of plants and effectiveness of the techniques.
- Earthworms present in soil have a direct impact on phytoremediation.

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