Abid Ali Ansari · Sarvajeet Singh Gill Ritu Gill · Guy R. Lanza Lee Newman *Editors*

Phytoremediation

Management of Environmental Contaminants, Volume 3



Phytoremediation

Abid Ali Ansari • Sarvajeet Singh Gill Ritu Gill • Guy R. Lanza • Lee Newman Editors

Phytoremediation

Management of Environmental Contaminants, Volume 3



Editors Abid Ali Ansari Department of Biology Faculty of Science University of Tabuk Tabuk, Saudi Arabia

Ritu Gill Centre for Biotechnology MD University Rohtak, Haryana, India

Lee Newman College of Environmental Science State University of New York Syracuse, NY, USA Sarvajeet Singh Gill Centre for Biotechnology MD University Rohtak, Haryana, India

Guy R. Lanza College of Environmental Science State University of New York Syracuse, NY, USA

ISBN 978-3-319-40146-1 ISBN 978-3-319-40148-5 (eBook) DOI 10.1007/978-3-319-40148-5

Library of Congress Control Number: 2014952730

© Springer International Publishing Switzerland 2016

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper

This Springer imprint is published by Springer Nature The registered company is Springer International Publishing AG Switzerland

Preface

"You must be the change you wish to see in the world"

Mahatma Gandhi

Volume 3 of this 5 volume series adds some more examples on phytoremediation of heavy metal and metalloid contaminants from terrestrial and aquatic ecosystems. In this volume, various studies on phytoremediation of mining areas, agricultural soil, crude oil contaminated soil, shooting range soil and industrial areas have been included. The importance of fast growing trees, wild grasses, aquatic weeds, ferns, hyperaccumulator and some transgenic plants in removal, degradation or stabilization of heavy metals and metalloid has been described. Information on heavy metal uptake, tolerance mechanisms and the role of metal transporters in phytoremediation have also been provided. The role of phytochelatins, biochar and green sorbents in phytoremediation of heavy metal contaminated soils and water has been described in different chapters of this volume. The chapters in volume 3 also illustrate how phytoremediation applications can serve as one of several useful components in the overall management and control of environmental contaminants especially heavy metals and metalloids. Volume 3 of this book series provides additional accounts of some selected phytoremediation research projects and case histories from specific sites and/ or laboratories. The editors and contributing authors hope that one result of publishing this book will be to provide a wide range of useful experimental data derived from global applications of phytoremediation. Hopefully, like the previous two volumes of this book series this volume can also provide new insights into the advantages and disadvantages of phytoremediation to manage the continuing threat of ecosystem degradation resulting from anthropogenic inputs of environmental contaminants.

Tabuk, Saudi Arabia Rohtak, India Rohtak, India Syracuse, NY, USA Syracuse, NY, USA Abid Ali Ansari Sarvajeet Singh Gill Ritu Gill Guy R. Lanza Lee Newman

Contents

Part I Phytoremediation of Heavy Metal Contaminants

1	Phytoremediation of Mining Areas: An Overview of Application in Lead- and Zinc-Contaminated Soils Tiziana Lai, Giovanna Cappai, and Alessandra Carucci	3
2	Phytoextraction of Heavy Metals by Fast-Growing Trees: A Review	29
3	Biological Approaches for Remediation of Metal-Contaminated Sites A.P. Pinto, A. de Varennes, M.E. Lopes, and D. Martins Teixeira	65
4	Biosorption of Heavy Metal from Aqueous Solutions Prayad Pokethitiyook and Toemthip Poolpak	113
5	Aquatic Macrophytes for the Removal of Heavy Metals from Coal Mining Effluent Virendra Kumar Mishra and Reetika Shukla	143
6	Heavy Metals Accumulation Ability of Wild Grass Species from Industrial Areas of Kazakhstan Saule Atabayeva	157
7	Bio-based Methods for Wastewater Treatment: Green Sorbents Alaa El Din Mahmoud and Manal Fawzy	209
8	Metal Hyperaccumulators: Mechanisms of Hyperaccumulation and Metal Tolerance Abdul Razaque Memon	239

Current Technical Perspective and Application of Aquatic Weeds in Phytoremediation Anand Mohan, S.M. Bhatt, Madhuri Girdhar, Geetanshu Goyal, Abid Ali Ansari, and Hasibur Rehman	269
Constructed Wetlands: Role in Phytoremediation of Heavy Metals Syed Shakeel Ahmad, Zafar A. Reshi, Manzoor A. Shah, and Irfan Rashid	291
Phytofiltration of Metal(loid)-Contaminated Water: The Potential of Native Aquatic Plants Paulo J.C. Favas, João Pratas, Manoj S. Paul, Santosh Kumar Sarkar, and M.N.V. Prasad	305
Phytoremediation of Heavy Metals Contaminated Soils Through Transgenic Plants Neerja Srivastava	345
Role of Phytochelatins in Phytoremediation of Heavy Metals Contaminated Soils Neerja Srivastava	393
Amina Hayyat, Maryam Javed, Iqra Rasheed, Shafaqat Ali,	
Heavy Metal Uptake and Tolerance Mechanisms of Serpentine Flora: Implications for Phytoremediation Mihiri Seneviratne, Sumedha Madawala, and Meththika Vithanage	439
Phytoremediation: Uptake and Role of Metal Transporters in Some Members of Brassicaceae Ritu Chaturvedi, Mayank Varun, and Manoj S. Paul	453
Phytoremediation of Shooting Range Soils Tharanga Bandara and Meththika Vithanage	469
t II Phytoremediation of Metalloid Contaminants	
Potential Promising Set of Plant–Microbe Interactions for the Revegetation of Open-Pit Mining and Smelting Areas in Brazil Wesley de Melo Rangel, Jerusa Schneider, Cláudio Roberto Fonsêca Sousa Soares, Rafael Dutra de Armas, Paulo Ademar Avelar Ferreira, Admir José Giachini, José Oswaldo Sigueira, and Fatima Maria de Souza Moreira	491
	of Aquatic Weeds in Phytoremediation Anand Mohan, S.M. Bhatt, Madhuri Girdhar, Geetanshu Goyal, Abid Ali Ansari, and Hasibur Rehman Constructed Wetlands: Role in Phytoremediation of Heavy Metals. Syed Shakeel Ahmad, Zafar A. Reshi, Manzoor A. Shah, and Irfan Rashid Phytofiltration of Metal(loid)-Contaminated Water: The Potential of Native Aquatic Plants Paulo J.C. Favas, João Pratas, Manoj S. Paul, Santosh Kumar Sarkar, and M.N.V. Prasad Phytoremediation of Heavy Metals Contaminated Soils Through Transgenic Plants Neerja Srivastava Role of Phytochelatins in Phytoremediation of Heavy Metals Contaminated Soils Neerja Srivastava Role of Biochar in Remediating Heavy Metals in Soil Amina Hayyat, Maryam Javed, Iqra Rasheed, Shafaqat Ali, Munazzam Jawad Shahid, Muhammad Rizwan, Muhammad Tariq Javed, and Qasim Ali Heavy Metal Uptake and Tolerance Mechanisms of Serpentine Flora: Implications for Phytoremediation Mihiri Seneviratne, Sumedha Madawala, and Meththika Vithanage Phytoremediation: Uptake and Role of Metal Transporters in Some Members of Brassicaceae Ritu Chaturvedi, Mayank Varun, and Manoj S. Paul Phytoremediation of Shooting Range Soils Tharanga Bandara and Meththika Vithanage t 11 Phytoremediation of Metalloid Contaminants Potential Promising Set of Plant–Microbe Interactions for the Revegetation of Open-Pit Mining and Smelting Areas in Brazil. Wesley de Melo Rangel, Jerusa Schneider, Cláudio Roberto Fonséca Sousa Soares, Rafael Dutra de Armas,

19	Phytoremediation of Arsenic-Contaminated Soils Using Arsenic	
	Hyperaccumulating Ferns	521
	Nabeel Khan Niazi, Safdar Bashir, Irshad Bibi,	
	Behzad Murtaza, Muhammad Shahid, Muhammad Tariq Javed,	
	Muhammad Bilal Shakoor, Zulfiqar Ahmad Saqib,	
	Muhammad Farrakh Nawaz, Zubair Aslam, Hailong Wang,	
	and Ghulam Murtaza	
20	Phytoremediation of Boron-Contaminated Sites	547
	Consuelo d.P. Rámila, Gonzalo E. Pizarro, and Carlos Alberto Bonilla	
Ind	ex	567

Contributors

Syed Shakeel Ahmad Department of Botany, University of Kashmir, Srinagar, India

Qasim Ali Department of Botany, Government College University Faisalabad, Faisalabad, Pakistan

ShafaqatAli Department of Environmental Sciences and Engineering, Government College University Faisalabad, Faisalabad, Pakistan

Abid Ali Ansari Department of Biology, Faculty of Science, University of Tabuk, Tabuk, Saudi Arabia

Danijela D. Arsenov Faculty of Sciences, Department for Biology and Ecology, University of Novi Sad, Novi Sad, Republic of Serbia

Zubair Aslam Department of Agronomy, University of Agriculture Faisalabad, Faisalabad, Pakistan

Saule Atabayeva Department of Biology and Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan

Tharanga Bandara Chemical and Environmental Systems Modeling Research Group, National Institute of Fundamental Studies, Kandy, Sri Lanka

Safdar Bashir Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

S.M. Bhatt Department of Biotechnology, Lovely Professional University, Jalandhar-Delhi, India

Irshad Bibi Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Southern Cross GeoScience, Southern Cross University, Lismore, NSW, Australia

MARUM and Department of Geosciences, University of Bremen, Bremen, Germany

Carlos Alberto Bonilla Department of Hydraulic and Environmental Engineering, Pontificia Universidad Católica de Chile, Santiago, Chile

Milan Borišev Faculty of Sciences, Department for Biology and Ecology, University of Novi Sad, Novi Sad, Republic of Serbia

Giovanna Cappai DICAAR, Department of Civil Environmental Engineering and Architecture, University of Cagliari, Cagliari, Italy

Alessandra Carucci DICAAR, Department of Civil Environmental Engineering and Architecture, University of Cagliari, Cagliari, Italy

Ritu Chaturvedi Department of Botany, St. John's College, Agra, India

Paulo J.C. Favas School of Life Sciences and the Environment, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal

Manal Fawzy Environmental Sciences Department, Faculty of Science, Alexandria University, Alexandria, Egypt

Paulo Ademar Avelar Ferreira Federal University of Santa Maria, Santa Maria, Rio Grande do Sul, Brazil

Admir José Giachini Federal University of Santa Catarina, Florianópolis, Santa Catarina, Brazil

Madhuri Girdhar Department of Biotechnology, Lovely Professional University, Jalandhar-Delhi, India

Geetanshu Goyal Department of Biotechnology, Lovely Professional University, Jalandhar-Delhi, India

Amina Hayyat Department of Environmental Sciences and Engineering, Government College University, Faisalabad, Pakistan

Muhammad Tariq Javed Department of Botany, Government College University, Faisalabad, Pakistan

Maryam Javed Department of Environmental Science and Engineering, Government College University, Faisalabad, Pakistan

Tiziana Lai DICAAR, Department of Civil Environmental Engineering and Architecture, University of Cagliari, Cagliari, Italy

M.E. Lopes Chemistry Department of Science and Technology School, Évora University, Évora, Portugal

HERCULES Laboratory, Évora University, Évora, Portugal

Sumedha Madawala Department of Botany, University of Peradeniya, Peradeniya, Sri Lanka

Alaa El Din Mahmoud Environmental Sciences Department, Alexandria University, Alexandria, Egypt

Abdul Razaque Memon Department of Molecular Biology and Genetics, Usak University, Usak, Turkey

Virendra Kumar Mishra Department of Environmental Science, Indira Gandhi National Tribal University, Amarkantak, India

Anand Mohan Department of Biotechnology, Lovely Professional University, Jalandhar-Delhi, India

Fatima Maria de Souza Moreira Federal University of Lavras, Lavras, Minas Gerais, Brazil

Behzad Murtaza Department of Environmental Sciences, COMSATS Institute of Information Technology, Vehari, Pakistan

Ghulam Murtaza Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Muhammad Farrakh Nawaz Department of Forestry and Range Management, Faculty of Agriculture, University of Agriculture Faisalabad, Faisalabad, Pakistan

Nabeel Khan Niazi Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Southern Cross GeoScience, Southern Cross University, Lismore, NSW, Australia

MARUM and Department of Geosciences, University of Bremen, Bremen, Germany

Nataša Nikolić Faculty of Sciences, Department for Biology and Ecology, University of Novi Sad, Novi Sad, Republic of Serbia

Saša Orlović Institute of Lowland Forestry and Environment, Novi Sad, Republic of Serbia

Slobodanka Pajević Faculty of Sciences, Department for Biology and Ecology, University of Novi Sad, Novi Sad, Republic of Serbia

Manoj S. Paul Department of Botany, St. John's College Agra, Agra, India

A.P. Pinto Chemistry Department of Science and Technology School, Évora University, Évora, Portugal

Institute of Mediterranean Agricultural and Environmental Sciences (ICAAM), Évora University, Évora, Portugal

Gonzalo E. Pizarro Department of Hydraulic and Environmental Engineering, Pontificia Universidad Católica de Chile, Santiago, Chile

Prayad Pokethitiyook Department of Biology, Faculty of Science, Mahidol University, Bangkok, Thailand

Toemthip Poolpak Department of Biology, Faculty of Science, Mahidol University, Bangkok, Thailand

M.N.V. Prasad Department of Plant Sciences, University of Hyderabad, Hyderabad, Telangana, India

João Pratas MARE—Marine and Environmental Sciences Centre, Faculty of Sciences and Technology, University of Coimbra, Coimbra, Portugal

Department of Earth Sciences, Faculty of Sciences and Technology, University of Coimbra, Coimbra, Portugal

Instituto de Geologia e Petróleo de Timor Leste, Díli, Timor-Leste

Consuelo d.P. Rámila Department of Hydraulic and Environmental Engineering, Pontificia Universidad Católica de Chile, Santiago, Chile

Wesley de Melo Rangel Federal University of Lavras, Lavras, Minas Gerais, Brazil

Iqra Rasheed Department of Environmental Sciences and Engineering, Government College University, Faisalabad, Pakistan

Irfan Rashid Department of Botany, University of Kashmir, Srinagar, India

Hasibur Rehman Department of Biology, Faculty of Science, University of Tabuk, Tabuk, Saudi Arabia

Zafar A. Reshi Department of Botany, University of Kashmir, Srinagar, India

Muhammad Rizwan Department of Environmental Sciences and Engineering, Government College University Faisalabad, Faisalabad, Pakistan

Zulfiqar Ahmad Saqib Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Santosh Kumar Sarkar Department of Marine Science, University of Calcutta, West Bengal, Kolkata, India

Jerusa Schneider University of Campinas, Campinas, São Paulo, Brazil

Mihiri Seneviratne Department of Botany, Faculty of Natural Sciences, Open University of Sri Lanka, Nawala, Nugegoda

Manzoor A. Shah Department of Botany, University of Kashmir, Srinagar, India

Muhammad Shahid Department of Environmental Sciences, COMSATS Institute of Information Technology, Vehari, Pakistan

Munazzam Jawad Shahid Department of Environmental Science and Engineering, Government College University Faisalabad, Faisalabad, Pakistan

Muhammad Bilal Shakoor Institute of Soil and Environmental Sciences, University of Agriculture Faisalabad, Faisalabad, Pakistan

Reetika Shukla Department of Environmental Science, Indira Gandhi National Tribal University, Amarkantak, India

José Oswaldo Siqueira Vale Institute of Technology, Sustainable Development, Nazaré, Brazil

Cláudio Roberto Fonsêca Sousa Soares Federal University of Santa Catarina, Santa Catarina, Brazil

Neerja Srivastava Department of Biochemistry, IBSBT, CSJM University, Kanpur, India

D. Martins Teixeira Chemistry Department of Science and Technology School, Évora University, Évora, Portugal

HERCULES Laboratory, Évora University, Évora, Portugal

A. de Varennes Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, University of Lisbon (TU Lisbon), Lisbon, Portugal

Mayank Varun Department of Botany, St. John's College Agra, Agra, India

Meththika Vithanage Chemical and Environmental Systems Modeling Research Group, National Institute of Fundamental Studies, Kandy, Sri Lanka

Hailong Wang Key Laboratory of Soil Contamination Bioremediation of Zhejiang Province, Zhejiang A & F University, Zhejiang, China

Milan Župunski Faculty of Sciences, Department for Biology and Ecology, University of Novi Sad, Novi Sad, Serbia

Part I Phytoremediation of Heavy Metal Contaminants

Chapter 1 Phytoremediation of Mining Areas: An Overview of Application in Lead- and Zinc-Contaminated Soils

Tiziana Lai, Giovanna Cappai, and Alessandra Carucci

1.1 Introduction

The metals concentration in soils is connected with natural and anthropogenic factors: metals are naturally present in soil in trace as a consequence of the decomposition of pedogenic substrate, while, anthropogenic activities such as emissions from the industrial areas, mine tailings, disposal of wastes, wastewater treatment, land fertilization and animal manures entail the release of metals into the environment, a large proportion of which are accumulated in soil [1–3]. On the basis of data reported by UNEP [4], mining is a significant contributor to the national economy in 158 countries worldwide.

Processing of lead and zinc metallic ores may involve a number of physical and chemical steps in order to separate the mineral resources from the less valuable material (gangue) [4]. Profitable recovery of lead and zinc ranges from about 3% of metal in ore, for large and easily accessed mines, to more than 10% in case of extremely costly and remote mines [5]. Minerals process, usually, produces several environmental impacts linked to each different stages of the process and generates large volumes of waste. Especially, waste rock and tailings represent a secondary source of pollutants that could contaminate soil, surface water and ground water even for hundreds of years after the mine closure. Moreover, the extent of contamination

G. Cappai • A. Carucci DICAAR, Department of Civil-Environmental Engineering and Architecture, University of Cagliari, Via Marengo 2, Piazza d'Armi, Cagliari 09123, Italy

T. Lai (🖂)

DICAAR, Department of Civil-Environmental Engineering and Architecture, University of Cagliari, Via Marengo 2, Piazza d'Armi, Cagliari 09123, Italy e-mail: lai.tiziana@gmail.com

IGAG-CNR, Institute of Environmental Geology and Geoengineering, Research National Council of Italy, Piazza d'Armi, Cagliari 09123, Italy e-mail: gcappai@unica.it; carucci@unica.it

due to the mobilization of metals can interest areas of hundreds of kilometres away from historical mining sites depending on site characteristics [6, 7].

Metals are included in lists of priority pollutants of US Environmental Protection Agency (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl and Zn) and of European Union with the Directive 2013/39/EU (Cd, Hg, Ni and Pb). These lists include both essential elements, toxic depending on the dose (e.g. Cr, Cu, Zn), and non-essential toxic elements, e.g. Hg and Pb [2, 8]. Different approaches can be considered for soil remediation: isolation, immobilization, toxicity reduction, physical separation and extraction. The selection of the most appropriate method depends on the site characteristics, nature of pollutants and their concentration. Physical and land-scape characteristics and entail high costs due to the wide areas involved [10–12]. Conversely, phytoremediation has been universally considered as a cost-effective technique that permits to restore biological activity and physical structure of soil (among others, [13–17]).

1.2 Lead and Zinc Mining Worldwide and Related Environmental Impacts

Mining activities produce several environmental impacts linked to each different stages of the mineral exploitation: starting from the exploration for the discovery of mineral deposits, the ore extraction and mineral processing until the mining closure and remediation of the site (Table 1.1).

The extent of impacts caused by mineral exploitation depends on site characteristics, amount of material handled, chemical composition of ore and surrounding rocks, extraction processes and technologies used to prevent or reduce the effects [4]. The excavation and the removal of vegetation related to exploration and operational phase are associated with metals contamination and erosion of soil [5]. The mineral processing includes physical and chemical methods. The physical methods present, generally, minor environmental impacts; chemical methods, due to the use of different reagents (sodium carbonate, sodium hydroxide, sulphuric acid, etc.) present instead a greater environmental impact [5].

Lead and zinc most often occur in association with the sulphide mineral group, in particular, galena (PbS) and sphalerite (ZnS). Other metals, such as copper, iron, mercury, arsenic, cadmium, silver and small quantities of gold are associated with sulphide ores [5]. Natural weathering process entails the oxidation of metal sulphide minerals in the host rock and the formation of sulphuric acid could occur prior to mining. However, the consequent release of acid and metal mobilization poses a limited threat to the environment. Conversely, extraction and mineral processing associated with mining activity expose larger volumes of sulphide rock material to weathering processes increasing the metal mobilization [18]. Especially after the mine closure, the runoff and leaching from waste rock and tailings increase the oxidation of remaining sulphides, through chemical, electrochemical and biological

Stages	Process	Impacts	Emission/waste
Extraction	Removal of ore material from a deposit and activities prior to beneficiation	Destruction of natural habitats and landscape Erosion caused by removal of vegetation Influence on hydrology around the excavated area Soil, water, and air pollution	Waste rock piles containing minerals associated with sulphide ores (chalcopyrite, pyrite, calcite, and dolomite) Wastewater from excavation phase Sediment run-off from mining sites. Acid mine drainage Wind dispersion of dust and greenhouse gas emissions
Beneficiation	Crushing, grinding, physical and chemical separation	Soil, water, and air pollution	Waste rock and tailings containing high concentration of metals and minerals, and toxic chemicals Wastewater containing dissolved solids and reagents Wind dispersion of dust and greenhouse gas emissions
Processing	Smelting and refining of concentrates	Air pollution	Emission of sulphur dioxide, arsenic, lead, cadmium, and other metals, dusts
Closure	Residues disposal	Contamination of surface, ground water, and air due to re-entrainment and/or subsequent deposition of particulates	Waste rock and tailings Acid mine drainage Leaching of pollutants from tailings Wind dispersion of dust from tailings

Table 1.1 Stages of mineral processing and main related impacts [4, 5]

reactions; furthermore, it could generate ferric hydroxides and sulphuric acid combined in acidic mine drainage that increases the leaching potential of metals and their transport into ground water, surface water and soil [18–20].

This phenomenon is site specific depending on many factors: climate conditions, neutralization capacity of local materials, etc. [18, 19, 21, 22]. The effects on the environment can be mitigated by both prevention and treatment options: minimization of oxygen diffusion, control of pH of mineral wastes, solidification of wastes, inhibition of iron and sulphur oxidizing bacteria [23]. Although modern mines are equipped and managed with technologies suitable to prevent or attenuate their impacts, countries with a long mining history may present, in most cases, significant

environmental impacts due to a poor management after mine closure [4, 24]. In fact, in modern mine, concentrations of As, Cd, Cu, Mn, Pb and Zn in tailings are as low as 1 g kg⁻¹ while in historic mine they can be greater than 50 g kg⁻¹ [10].

Numerous authors have evaluated the environmental contamination in the surrounding area of mining sites in different countries (among others, [25-33]). Recently, the spatial variability of Pb, Zn and Cd pollution in the mining sites of Bama mine (Iran) and surrounding urban areas has been evaluated by Dayani and Mohammadi [34]. Candeias et al. [20] assessed the levels of soil contamination in the Aljustrel mine (SW Portugal), with the aim to understand the partitioning and availability of pollutants in soil. The results showed a severe contamination (maximum concentration of Pb and Zn of 20000 mg kg⁻¹). Pb and Zn contamination due to former mining and smelting carried out in Plombières and La Calamine (Belgium) was evaluated by Cappuyns et al. [35].

The effect of mining and metallurgical activities in the neighbourhood of the Bolesław Mine and Metallurgical Plant in Bukowno (Poland) was evaluated by Agnieszka et al. [3] by germination inhibition and luminescence inhibition test for the assessment of ecological risks in soil and water. Impact of Pb and Zn mining activity on superficial sediments of Lake Kalimanci (FYR Macedonia) related to the weathering of tailings dam material was studied by Vrhovnik et al. [36].

The metals accumulation in soil determines direct and indirect effect on biotic communities. Metal accumulation in plants alters seed germination, plant growth, absorption and transport of essential elements. In addition, it can cause chlorosis, photosynthesis inhibition and mortality. A study done on wild rodents and plants, reported negative effects, such as loss of diversity of the biotic communities, due to metals bioaccumulation [37]. Moreover, soil contaminated from a Pb and Zn mine showed a decrease on both the biomass and diversity of the bacterial community in soil [38].

The metal fraction that, within a given time span, is either available or can be made available for uptake by plant in addition to the total metals concentration in soil, must be evaluated and also the metal chemical speciation must be identified in order to define the most suitable remediation technology [9, 39]. The speciation of trace metals depends on the physical and chemical characteristics of the soil: pH, redox potential, organic, carbonate, clay and oxide contents [9].

With the aim to predict the mobility and availability of metal in soil, different extraction methods have been developed [39, 40].

1.3 Phytoremediation Technologies Applied in Pb/Zn Mining Areas

Phytoremediation is a technology based on the capacity of plants to accumulate both metals which are essential elements for their growth (i.e. Zn) and metals which have no known biological function (i.e. Pb) [8, 41]. Technologies applicable

for cleanup of Pb- and Zn-contaminated soils include phytoextraction (metals removal from soil and their concentration in the harvestable parts of plants) and phytostabilization (reduction of the mobility and bioavailability of metals in the environment) [41–43]. Plants suitable in phytoextraction should be tolerant to high metal concentration in soil, have the capability to accumulate great levels of metal in the harvestable part, have high growth rate and biomass production and finally have an extended root system [44].

In case of phytostabilization plants should be tolerant to the soil conditions, have high growth rate, provide a dense ground cover and have an extended root system. Moreover, plants must concentrate contaminant in a greater extent in root in comparison to aerial part [16]. Plant species that are capable of colonizing soils highly polluted by metals are defined metallophyte and pseudometallophyte species. Metallophytes, including hyperaccumulators, are endemic plant of natural mineralized soils which have developed physiological mechanisms of resistance and tolerance to the high metal concentration in soil and are generally characterized by a reduced production of biomass. Pseudometallophytes are native species common also in non-metalliferous soil which, due to selective pressure, are capable of surviving in soils highly polluted by metals [17].

Over 400 hyperaccumulator plants have been identified, some of these species, belonging to the Aceraceae, Brassicaceae, Caryophyllaceae, Cistaceae, Dichapetalaceae, Plumbaginaceae, Poaceae, Polygonaceae and Violaceae, in particular, were demonstrated capable of accumulating Pb and/or Zn [45-48]. Plants species are considered hyperaccumulators if metal concentration in shoots is >1000 and >10000 mg kg⁻¹ of dry weight for Pb and Zn, respectively, when grown in metal-rich soils [49]. Thlaspi caerulescens, common in Western and Central Europe, can accumulate a maximum of 4% of Zn in its dry matter and a less extent of Cd and Pb [46]. Thlaspi rotundifolium ssp. cepaeifolium, from a Pb and Zn mining area in Northern Italy has accumulated Pb at about 0.8% of dry weight [45]. Recently, van der Ent et al. [50] has proposed a critical review on criteria commonly used to delimit hyperaccumulation of some metals and indicated lower limit. For instance, a limit lowered to 3000 mg kg⁻¹ of dry weight was proposed for Zn. On the other side, excluders are plant species able to accumulate metals in roots limiting their transport into aerial parts, these plants are ideal candidate for phytostabilization process. Indicators accumulate metals in their aerial parts generally in proportion to the metal concentration in soil [51].

Previous investigations have demonstrated the accumulation potential of tree species, such as *Salix* spp., *Populus* L. and *Betula* L., when growing on metal-contaminated soils [43, 52–55]. Potential to accumulate metals in harvestable parts of *Salix* spp. (*Salix purpurea* L., *Salix caprea* L. and *Salix eleagnos* Scop.) collected from abandoned sulphide mine dumps has been evaluated [56]. The metal accumulation capacity evaluated by translocation factor (TF), ratio between metal concentration in shoots and metal concentration in roots, has shown significant differences among the species studied: *S. purpurea* was able to uptake and translocate Pb from roots to shoots (TF=3.42) while *S. caprea* demonstrated similar ability for Zn (TF=3.48), considering a soil with a mean Pb and Zn concentration of about 9600 and 1250 mg kg⁻¹, respectively. The metal translocation ability, combined with high

biomass production makes these species suitable for phytoremediation and phytoextraction, in particular [56, 57].

Even agricultural and ornamental species have the capability to concentrate metals together with a high biomass production. Brassica napus, Brassica juncea, Helianthus annuus and Zea mays have been considered among others; generally, these species can be applied in a multi-metal-contaminated soil [58-60]. In case of use of agricultural species, some factors have to be taken into account: adaptability at the local climate conditions and soil agronomic properties, and tolerance to metal concentration in soil of the species chosen. The ornamental species Mirabilis *jalapa* L. has demonstrated its capacity to accumulate 1500 mg kg⁻¹ of Pb in roots and about 400 mg kg⁻¹ in the aerial part of the plant, from a soil with a Pb concentration of about 5500 mg kg⁻¹ [61]. In case of phytoremediation of mining areas, native plants are preferable in comparison to introduced or invasive species, in order to reduce possible impact on the ecosystem [10, 62, 63]. Moreover, native plant species growing on mine tailings demonstrated a better tolerance to local conditions (climate, contamination and nutrient deficiency, etc.) [17, 64, 65]. Recently, different studies, summarized in Table 1.2, have been conducted in Pb and Zn mining areas in order to identify native plant species potentially relevant in phytoremediation.

In natural or continuous phytoremediation, plants with a TF>1 are considered suitable species for phytoextraction, while species with a TF<1 are generally considered suitable for phytostabilization and revegetation process. In addition, with the aim to modify accumulation characteristics of plants, soil amendments can be applied either to increase metal availability in soil (e.g. chelating agents or acidifying amendments), in case of assisted phytoextraction, or improve soil agronomic proprieties (e.g. fertilization), in case of aided phytostabilization [41, 66]. A field experiment was conducted by Zhuang et al. [67] with the aim to evaluate the effect of EDTA (ethylenediaminetetraacetic acid) in phytoextraction. Three plants were tested: Viola baoshanensis, Vertiveria zizanioides and Rumex K-1 (Rumex patien $tia \times R$. Timschmicus). Among the species tested, V. baoshanensis showed high potential for phytoremediation, and the application of EDTA enhanced Pb and Zn phytoextraction rates from 0.01 to 0.19%, and 0.17 to 0.26%, respectively. However, in assisted phytoextraction the chemical treatments can become a secondary cause of pollution. In fact, chelating agents, such as EDTA, are slowly biodegradable and increase the leachable metal fraction into ground water [68, 69]. In order to overcome these effects, biodegradable chelating agents should be applied [70].

In an assisted phytoextraction experiment in pots, Cao et al. [71] compared Pb and Zn phytoextraction by *M. jalapa*, using EDDS ([*S*,*S*]-ethylenediaminedisuccinic acid) and MGDA (methylglycinediacetic acid) in two different dosages (4 and 8 mmol kg⁻¹ of soil). Both chelating agents demonstrated to increase Pb accumulation in leaves as well as improve bacterial activity in the soil. In the case of Zn, metal accumulation was independent from chelating agents application. However,

			Metal concentr in soil (1 [mg kg ⁻	nean)	TF		
Plant species	Mine	Location	Pb	Zn	Pb	Zn	Reference
Achyrocline alata (Kunth) DC.	Hualgayoc	Peru	16060	28058	1.5	2.0	Bech et al. [103] ^a
Ageratina sp.	Hualgayoc	Peru	16060	28058	0.4	0.6	Bech et al. [103] ^a
Aster gymnocephalus A. Gray	Santa Maria	Mexico	4183	4546	2.0	20.5	Sánchez-López et al. [104]
Betula celtiberica	Rubiales	Spain	3000	20000	0.2	0.8	Becerra-Castro et al. [95]
Bidens triplinervia L.	Hualgayoc	Peru	13105	28393	0.13	0.16	Bech et al. [105]
Brickelia veronicifolia (Kunth) A. Gray	San Francisco	Mexico	1923	4745	0.6	1.4	Sánchez-López et al. [104]
Brickelia veronicifolia (Kunth) A. Gray	Santa Maria	Mexico	4183	4546	1.3	4.2	Sánchez-López et al. [104]
Cistus populifolius L.	Caveira	Portugal	4245	494	0.1	5.0	Abreu et al. [106]
Cistus populifolius L.	Chança	Portugal	141	66	0.11	2.53	Abreu et al. [106]
Cistus salviifolius L.	Campo Pisano	Italy	3260	12000	2.0	2.2	Cao et al. [107]
Cistus salviifolius L.	Chança	Portugal	141	66	0.2	2.93	Abreu et al. [106]
Cistus salviifolius L.	São Domingos	Portugal	4853	605	0.54	2.14	Abreu et al. [108]
Cistus salviifolius L.	Caveira	Portugal	7416	357	0.1	2.72	Abreu et al. [108]
Cistus salviifolius L.	Caveira	Portugal	4245	494	0.1	2.17	Abreu et al. [106]
Cistus salviifolius L.	São Domingos	Portugal	5901	294	0.34	2.59	Abreu et al. [106]
Cistus imes hybridus	Caveira	Portugal	4245	494	0.11	5.32	Abreu et al. [106]
Cistus × hybridus	Chança	Portugal	141	66	1.5	2.74	Abreu et al. [106]
Cortaderia hapalotricha Pilg.	Hualgayoc	Peru	16060	28058	1.7	1.2	Bech et al. [103] ^a

 Table 1.2
 Native plants species in phytoremediation experiment in mine soil contaminated by Pb and Zn (TF=translocation factor)

(continued)

			Metal concentri in soil (r [mg kg ⁻¹	nean)	TF		
Plant species	Mine	Location	Pb	Zn	Pb	Zn	Reference
Crotalaria pumila Ortega	Santa Maria	Mexico	4183	4546	1.1	11.6	Sánchez-López et al. [104]
<i>Cuphea</i> <i>lanceolata</i> Aiton	San Francisco	Mexico	1923	4745	0.6	6.7	Sánchez-López et al. [104]
Cytisus scoparius	Rubiales	Spain	3000	20000	0.2	0.4	Becerra-Castro et al. [95]
<i>Dalea bicolor</i> Humb. & Bonpl. Ex Willd.	San Francisco	Mexico	1923	4745	0.6	2.3	Sánchez-López et al. [104]
<i>Dalea bicolor</i> Humb. & Bonpl. Ex Willd.	Santa Maria	Mexico	4183	4546	0.9	3.3	Sánchez-López et al. [104]
Debregeasia orientalis	Beiya	China	2217	240	0.93	0.83	Liu et al. [109]
Dichondra argentea Willd.	San Francisco	Mexico	1923	4745	0.6	3.4	Sánchez-López et al. [104]
Dichondra argentea Willd.	Santa Maria	Mexico	4183	4546	0.8	1.3	Sánchez-López et al. [104]
<i>Epilobium denticulatum</i> Ruiz & Pav.	Hualgayoc	Peru	10128	23678	1.1	1.5	Bech et al. [103] ^a
Festuca rubra	Rubiales	Spain	3000	20000	0.10	0.2	Becerra-Castro et al. [95]
Flaveria trinervia	Santa Maria	Mexico	4183	4546	1.0	10.9	Sánchez-López et al. [104]
Gnaphalium sp.	Santa Maria	Mexico	4183	4546	1.6	20.8	Sánchez-López et al. [104]
Hyparrhenia hirta	Cartagena-La Union	Spain	4200	15000	0.8	0.3	Conesa et al. [110]
<i>Juniperus</i> sp.	San Francisco	Mexico	1923	4745	1.1	17	Sánchez-López et al. [104]
Pteridium sp.	San Francisco	Mexico	1923	4745	0.2	0.2	Sánchez-López et al. [104]
<i>Ruta graveolens</i> L.	San Francisco	Mexico	1923	4745	1.0	2.5	Sánchez-López et al. [104]
Scrophularia canina subsp. bicolor	Campo Pisano	Italy	3260	12000	0.8	1.1	Cao et al. [107]
Senecio sp.	Hualgayoc	Peru	13105	28393	9.4	4.7	Bech et al. [105]
<i>Taraxacum</i> officinale Weber	Hualgayoc	Peru	14197	25829	0.6	0.4	Bech et al. [103] ^a

Table 1.2 (continued)

(continued)

			Metal concentra in soil (n [mg kg ⁻¹	nean)	TF		
Plant species	Mine	Location	Pb	Zn	Pb	Zn	Reference
Tephrosia candida	Beiya	China	2207	256	0.85	0.77	Liu et al. [109]
<i>Teucrium flavum</i> L. subsp. glaucum	Campo Pisano	Italy	3260	12000	1.6	0.7	Cao et al. [107]
<i>Trifolium repens</i> Walter	Hualgayoc	Peru	10128	23678	1.5	1.3	Bech et al. [103] ^a
Viguiera dentata (Cav.) Spreng.	San Francisco	Mexico	1923	4745	0.5	0.9	Sánchez-López et al. [104]
Viguiera dentata (Cav.) Spreng.	Santa Maria	Mexico	4183	4546	0.6	2.0	Sánchez-López et al. [104]
Zygophyllum fabago	Cartagena-La Union	Spain	4800	13000	0.7	1.5	Conesa et al. [110]

Table 1.2(continued)

^aData referring to the substrate having the higher metal concentrations

both EDDS and MGDA demonstrated to be toxic to the plant causing death at maximum dose. Response of treatment with chelating agents seems to be related to the dosages applied [72–75].

The application of complementary techniques such as additives application and fertilization could improve phytostabilization results [76, 77]. The organic amendments, as compost, increase the content of essential nutrients of soil (C, N, P, K), which improve plant growth and stimulate the microbial activities. The effectiveness of these treatments for the reduction of soil risks have been confirmed by ecotoxicological tests with bacteria *Vibrio fischeri*, crustaceans *Daphnia magna* and *Thamnocephalus platyurus* and earthworm *Eisenia fetida* tests [78, 79].

A greenhouse experiment was conducted by Lee et al. [80] to evaluate the effect of four different amendments (bone mill, bottom ash, furnace slag and red mud) as immobilizing agents and two Korean native plant species, *Miscanthus sinensis* and *Pteridium aquilinum*, in aided phytostabilization of Pb and Zn mine tailings. Results of the study suggest that *M. sinensis* is appropriate for phytostabilization, since it accumulated heavy metals mainly in the root, and had lower translocation factors compared with *P. aquilinum*; furthermore, amendments such as furnace slag and red mud are effective at reducing the availability and mobility of metals. Recently, phytostabilization experiments have been carried out in field with the use of native species, selected on the basis of their ability to survive and regenerate in the local environment.

The area of the experiments performed by de la Fuente et al. [81], was located downstream the Aznalcóllar mine (Spain) [82], previously object of different phytoremediation experiments [83]. Native species (*Retama sphaerocarpa, Tamarix gallica, Rosmarinus officinalis* and *Myrtus communis*) were grown under natural conditions, without any agricultural practice or irrigation system, in soil with a maximum metal concentration of about 839 and 1617 mg kg⁻¹ for Pb and Zn, respectively. The results permitted to identify the *R. sphaerocarpa* as the most adequate plant species for soil restoration. At the end of the experiment, *R. sphaerocarpa* showed the highest percentage of plant survival (44%), the ability to grow in soils with poor agronomic properties and acidic conditions, and the lower bioconcentration factor (i.e. metal concentration in shoot tissues versus total metal concentration in soil) equal to 0 and 0.19 for Pb and Zn, respectively.

Results from an application of P fertilizers (phosphate rock, calcium magnesium phosphate and single superphosphate) in field plots planted with *Brassica chinensis* L. *campestris* indicate that these amendments induced immobilization of metals such as Pb, Cd and Zn [84].

The phytostabilization experiment performed in the tailings dam of Campo Pisano (Sardinia, Italy), consisted in the use of different soil amendments, compost, chemical fertilizer and zeolites, used singly or in combination. In general, all amendments reduced the bioavailable metal fraction; in particular, compost proved to be the best amendment in the long-term for plant growth. Among the plant species tested (*Scrophularia canina* subsp. *bicolor Greuter* and *Pistacia lentiscus*) *P. lentiscus* appears to be the most suitable species for phytostabilization and revegetation, both for its resistance to metals and high phytomass production [85].

Galende et al. [86] evaluated the application of combined organic amendments (cow slurry, poultry manure and paper mill sludge mixed with poultry manure) in a phytostabilization experiment on an abandoned Pb and Zn mine located in the province of Biscay (Basque Country, Spain) with *Festuca rubra L*. species. Amendment application demonstrated to promote biomass production in *F. rubra* and caused a reduction in bioavailable Pb and Zn in soils. Further investigations focusing on phytoremediation of Pb and Zn mine areas have been conducted also by applying non-native species as reported in Table 1.3.

An additional aspect to be considered is that plants play an important role in reducing dispersion of soil-contaminated particles from mine tailings caused by atmospheric agents. Recently, the role of leaves of plants growing spontaneously on mine tailings acting as a barrier for the dispersion of particles containing potentially toxic elements has been evaluated [87]. Comprehensive reviews, summarizing the most important aspects of phytoremediation processes and physiological mechanisms of metal accumulation in plants are available (Table 1.4).

Metecy CT MODT								
		Pb in soil	Zn in soil Pb in soil	Pb in soil	Zn in soil	Details		
						on		
		Total	Total	Extractable	Extractable Extractable extraction	extraction		
Plant species	Location	(mg kg ⁻¹)	(mg kg ⁻¹)	$(mg\ kg^{-1})\ \left(mg\ kg^{-1}\right)\ \left(mg\ kg^{-1}\right)\ \left(mg\ kg^{-1}\right)\ \left(mg\ kg^{-1}\right)\ $		agent	Amendments	Reference
Triticum	Příbram (Czech	3035	4900	266	2925	Acetic	Digestate (biowaste anaerobic	García-
aestivum L.	Republic)					acid	fermentation)	Sánchez
							Fly ash (wood chip combustion)	et al. [111]
							$(NH_4)_2SO_4$	
Mirabilis jalapa	Montevecchio-	5357	1767	3426	432	EDTA	Clinoptilolite	Lai et al.
L.	Ingurtosu (Italy)						Clinoptilolite NH4 ⁺⁻ charged	[61]
							Clinoptilolite CO ₂ -charged	
Zygophyllum	Cartagena-La	I	I	277	495	DTPA	Pig manure + marble waste	Zornoza
fabago L.	Unión (Spain)							et al. [112]
Piptatherum							Sewage sludge + marble waste	
miliaceum (L.)								
Coss.								
Dittrichia								
viscosa (L.)								
Greuter								
Phragmites								
australis (Cav.)								
Trin. ex Steud								
Helichrysum								
aecumpens DC.								
Sonchus								
tenerrimus L.								

 Table 1.3
 Assisted phytoremediation experiments in mine soils contaminated by Pb and Zn

(continued)

(continued)
1.3
Table

Iable 1.3 (continued)	ued)							
		Pb in soil	Pb in soil Zn in soil Pb in soil		Zn in soil	Details		
		Total	Total	Extractable	Extractable Extractable extraction	on extraction		
Plant species	Location	$(mg kg^{-1})$	$(mg kg^{-1})$	$(mg kg^{-1})$ $(mg kg^{-1})$ $(mg kg^{-1})$	$(mg kg^{-1})$	agent	Amendments	Reference
Vertiveria	Lechang (China)	096	1050	119	93	DTPA	EDTA (ethylenediaminetetracetic acid)	Zhuang
zizanioides								et al. [113]
Dianthus	1							
chinensis								
Rumex K-1								
(Rumex								
$upatientia \times R$.								
timschmicus)								
Rumex crispus								
Viola								
baoshanensis								
Sedum alfredii								
Brachiaria	Biscay (Spain)	4166	15277	I	I	I	EDTA (ethylenediaminetetracetic acid)	Santos
decumbens							EDDS (ethylenediaminedisuccinate)	et al. [114]
Vetiveria	Lechang (China)	1155	1583	361	834	DTPA	Manure compost	Chiu et al.
zizanioides								[115]
Phragmities australis							Sewage sludge	
Helianthus	Bama (Iran)	1564	2739	29	182	DTPA	DTPA (diethylenetriaminepentaacetic	Solhi et al.
annuus						1	acid)	[116]
Brassica napus							Composted manure	
							Sulphuric acid	

	177 161
187	331 18