# Utilizing Mediterranean Plants to Remove Contaminants

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The use of contaminated soils in food production imposes the need for the reduction in heavy metals concentrations, using various techniques, in order to eliminate the toxic effects of pollution and ensure safety in the consumption of agricultural products. Phytoremediation is a promising, effective, and publicly acceptable method to remove soils' toxicity. The Mediterranean basin is a region of distinct climatic conditions with temporal variability and great floristic heterogeneity. Due to the high variability in landscapes paired with the warm, dry summers and cool, wet winters, the Mediterranean hosts significant plant diversity, including numerous endemic and rare plant species

Keywords: soil pollution ; heavy metals ; soil contamination ; phytoremediation ; flora

# 1. Introduction

In recent decades, there has been a rising demand for remediation technologies as the levels of pollution have grown considerably [1][2]. Contaminants are present in hazardous amounts in many parts of the world, posing a severe health risk for ecosystems and all levels of the food chain. Contamination by heavy metals is of particular concern as their nondegradable and persistent qualities make them difficult to manage. Their accumulated effect in both the environment and at the organism level amplifies the need for taking active measures for their mitigation <sup>[3]</sup>. Heavy metals in soils are normally present in trace amounts as they derive naturally from sources such as the weathering of parent materials, erosion, volcanic eruptions, and forest fires [4][5]. However, anthropogenic activities over the years have added large amounts of heavy metals to the environment, and thus they have clearly exceeded the previously low quantities in which they were encountered. Heavy urbanization and industrialization, intensive mining and smelting activities, and the overuse of pesticides and other chemical additives in the agricultural sector have had a huge input into the degradation of vast areas by heavy metal contamination <sup>[6][]</sup>. According to a review article by Panagos et al. <sup>[8]</sup>, an impressive number of 1,170,000 European sites were suspected as being contaminated until 2011. In the same study, it was reported that a large part of the aforementioned contamination was due to heavy metals [8]. There have been many reports of contaminated and/or degraded land in need of restoration in Mediterranean Europe. There are a number of studies indicating sites with elevated concentrations of heavy metals in Spain (e.g., in the Valencia and Castellón Provinces and Segura river valley, Alicante), Portugal (e.g., Esteiro de Estarreja), Italy (e.g., Apulia region), Greece (e.g., Thriasian Plain, Lavrio, Almyros region, Thasos Island, Chalkidiki, Kozani), and Cyprus (e.g., Yedidalga mine harbor) [9][10][11][12][13][14][15].

A number of technologies emerged to meet the need for soil remediation in past decades, but the task has proven to be rather challenging. Conventional methods of remediation (chemical and physical), although possibly effective at small scale, have been deemed lacking in terms of sustainability as they come with a large cost and have adverse effects themselves. The general turn towards more sustainable, eco-friendly technologies has allowed for the development of biological remediation methods, such as phytoremediation. This is a technology that constitutes a nature-based solution, which agrees with the goals set by the current European Guidelines. However, phytoremediation research is required as the effectiveness of the technique is highly dependent on the plant species used. Identifying the correct species, specifically adapted and tolerant to the environmental conditions of the contaminated site, among other factors, is one of the core parameters that will determine the success of phytoremediation projects <sup>[6][15][16]</sup>.

The Mediterranean basin is a region of distinct climatic conditions with temporal variability and great floristic heterogeneity. Due to the high variability in landscapes paired with the warm, dry summers and cool, wet winters, the Mediterranean hosts significant plant diversity, including numerous endemic and rare plant species [17][18][19][20][21].

Metalliferous soils are abundant in the region and so native plant species are expected to be more tolerant than most to metal stress. In fact, as exemplified by Reeves et al. (2018), the Mediterranean basin is considered to be a source for nickel hyperaccumulating species <sup>[18]</sup>. Moreover, some examples of the metalliferous soils in the Mediterranean region are

the area of Stratoni in Chalkidiki, Northern Greece (Pb, Zn, Ag) <sup>[2]</sup> and the area of Castellón, a province of the Valencian Mediterranean region (Pb, Zn, Cd, Cu) <sup>[9]</sup>.

Furthermore, it is important to acknowledge that the use of plant-based remediation is not limited to anthropogenically contaminated areas and is applicable to marginal lands in general. An issue that has been of emerging concern is the management of land damaged by fires. Such areas, which are unfortunately rising in number each year, have a high metal content and are in need of restoration. Mediterranean summers are known to be fire-prone and so phytoremediation may be a valuable tool for treating the affected areas <sup>[2]</sup>. Notably, phytoremediation may be an even more attractive approach as, when associated with other technologies (e.g., biofuel production, agromining, etc.), it forms a circular economy model <sup>[6][22]</sup>.

# 2. Phytoremediation of Heavy Metals

## 2.1. Toxic Metals

A subject of scientific and technological progress is phytoremediation and, more specifically, the phytoremediation of toxic metals in the environment. The use of biological processes to overcome environmental problems and the ability to break down undesirable substances is become more important. A serious impact of the global industrial activity is the extensive accumulation of heavy metals in soils, which has become very serious. This accumulation of toxic metals in the environment has resulted from various types of waste and pollutants, such as mining waste, fertilizers, paper mills, and various toxic elements from emissions in the atmosphere. Unfortunately, the concentration of toxic metals found in polluted soils is often considerably greater than that which is required to exert a toxic effect on the majority of higher plants (e.g., the hyperaccumulation threshold values are set at 100  $\mu$ gg<sup>-1</sup> for Cd, Se, and Tl; 300  $\mu$ gg<sup>-1</sup> for Co, Cr, and Cu; 1000  $\mu$ gg<sup>-1</sup> for As, Ni, and Pb; 3000  $\mu$ gg<sup>-1</sup> for Zn; and 10,000  $\mu$ gg<sup>-1</sup> for Mn) <sup>[2]</sup>. Another unsettling fact is the certainty that toxic metals can affect the biosphere for extremely long periods, polluting the water table through the soil layers. Hence, the use of edible plants contaminated with high levels of heavy metals can pose a serious threat to the health of humans and animals <sup>[23]</sup>.

#### 2.2. Phytoremediation

The idea of using plants to clean contaminated areas is not new. About 300 years ago, plants were proposed for use in wastewater treatment, and in the late 19th century, *Thlaspi caerulescens* and *Viola calaminaria* were the first plants reported to accumulate high levels of minerals in their leaves <sup>[24][25]</sup>. Then, in 1935, Byers reported that plants of the genus *Astragalus* were able to accumulate up to 0.6% of Selenium in their dry aboveground biomass <sup>[26][27]</sup>. A decade later, in 1948, the Italian researchers Minguzzi and Vergnano recognized the plant *Alussum bertolonii* as a nickel super-accumulator. This fact was forgotten until 1977, when Robert Brooks, a scientist at Massey University in New Zealand, reported similar findings <sup>[26][27][28][29]</sup>, and the idea of using plants to remove metals from contaminated soils was reintroduced and developed by Utsunamyia in 1980 and Chaney in 1983. The first field application of cadmium and zinc phytoaccumulation took place in 1991 <sup>[26][27]</sup> and in the same year the name "phytoremediation" was coined.

The term phytoremediation comes from the Greek word "plant" and from the Latin word "remedium", which means healing. The term phytoremediation can be defined as the process of repairing a contaminated area using plants that are capable of removing or modifying a wide range of hazardous substances, and a range of organic and inorganic pollutants from soils, water (surface and underground) sediments, and the atmospheric air through physical, chemical, and biological processes of plants [30][31][32][33][34][35].

Phytoremediation is classified to the category of biological restoration technologies used by living organisms (such as plants, seaweeds, microalgae, bacteria, and fungi) as biodegraders of pollutants. It is commonly used in combination with other recovery technologies to improve the effectiveness of the recovery of infected areas. However, research has shown that it can also be used autonomously to rehabilitate soils and waters characterized by low or moderate levels of pollution [36][37][38][39]. This technology is suitable for infected areas that have been contaminated with more than one type of pollutant where the use of other conventional technologies is economically unsustainable <sup>[40]</sup>.

More specifically, phytoremediation technology is an in situ restoration technique. For example, in the case of contaminated soils, excavation and soil transfer to another area is not required and restoration is performed on site. It is based on the collaboration or individual ability of genetically modified or non-genetically modified plants and soil microorganisms that function naturally as biodegraders of pollutants. Phytoremediation can remove organic and inorganic pollutants such as petroleum hydrocarbons, chlorinated solvents, pesticides, explosives, heavy metals, nutrients, and radionuclides [41][42][43][44][45].

In addition, it is worth mentioning a new application of phytoremediation for the restoration and improvement of soils burdened with high salinity concentrations. As is well known, salinity occurs in large parts of the world, which cover up to 20% of the total cultivated area. In the Mediterranean region alone, 80 million hectares of land are burdened with high salt concentrations  $\frac{[46][47][48]}{10}$ . The application of the phytoremediation technique in this case is based on the use of salinity-resistant plants, which, through their roots, can enhance the solubilization of soil CaCO<sub>3</sub> by providing calcium (Ca+<sup>2</sup>) to replace Na+ at the cation exchange sites, resulting in its infiltration into the deeper layers of the soil  $\frac{[49][50][51][52][53][54][55]}{10}$ .

Thus, although organic pollutants can be degraded either in plant tissue or with the help of soil microorganisms, heavy metals require either natural removal or immobilization. As a consequence, two distinct strategies have been developed for the phytoremediation of soils contaminated with heavy metals: phytoaccumulation and phytostabilization. The first method aims to remove the dirt using plants that have the genetic potential to absorb and accumulate the dirt in their tissues, whereas the second aims to immobilize soil contaminants using metal-resistant plants that have an extensive root system and can immobilize contaminants in the rhizosphere by providing soil cover and preventing corrosion by water and air [56].

# 2.3. Types of Phytoremediation

This technique involves a number of different methods that can lead to decomposition, removal (through accumulation or dispersion), or immobilization of the contaminant  $\frac{[57][58][59][60][61][62][63]}{100}$ :

- Decomposition (for destruction or conversion of organic pollutants);
- Rhizodegradation or enhanced rhizosphere biodegradation: enhances the biodegradation of pollutants by microorganisms in the rhizosphere;
- Phytodegradation: uptake of the pollutant and its metabolism in root, stem, or leaf tissues;
- Accumulation (for retention or removal of mainly metallic and organic pollutants);
- Phytoextraction or phytoaccumulation: uptake and accumulation of pollutant for disposal;
- Rhizofiltration: adsorption of the pollutant by the roots for retention and/or removal;
- Dispersion (to remove organic and/or inorganic pollutants into the atmosphere);
- Phytovolatilization: uptake and evaporation of pollutants;
- Immobilization (for retention of organic and/or inorganic pollutants);
- Phytostabilization: immobilization of the pollutant in the soil;
- Hydraulic Control: control of groundwater flow through the uptake of water by plants.

## 2.4. Advantages and Disadvantages

Phytoremediation technology is relatively inexpensive. Following the selection and planting of plants, the cost is usually related to harvesting and crop management (e.g., weed control, watering, fertilizing, pruning, fencing, etc.). The application of the method is simple; no specialized mechanical equipment is required and it functions as an autonomous system because the energy used for the growth of the plants is provided by the sun (solar energy). It is one of the most economically viable options compared to other conventional technologies currently in use, which usually require much higher investment capital, special mechanical equipment, large amounts of energy consumption (e.g., fuel), and skilled labor <sup>[64][65]</sup>.

One of the most important advantages of this method (**Table 1**), apart from the low cost, is the enrichment of the soil with organic substances and microorganisms, which improve and protect the physicochemical and biological qualities of the soil and water  $\frac{[66][67]}{1}$ . Moreover, it protects the soil from corrosion that can be caused by wind and water. Phytoremediation can replace the use of fossil fuels for energy production, and be used for metal recycling because the combustion of plant biomass produces ash residues as a by-product, which contain metals that can be recovered after special treatment. Another important advantage is that it can reduce greenhouse gas emissions by storing large amounts of carbon in the soil and plants. When the biomass produced by the plants is collected and burned, no more CO<sub>2</sub> is introduced into the air than that originally assimilated by the plants during their growth.

Table 1. Advantages and disadvantages of phytoremediation [68][69][70][71][72][73].

Advantages	Disadvantages
Low cost. Minimum required nutrient and energy inputs.	Time consuming. Slow recovery rate can take up to 10 years.
More environmentally friendly than other conventional mechanical techniques.	Restricted to polluted areas with low to moderate levels of pollution.
It can be used to produce energy from the biomass of plants that is produced.	Low biomass production and small plant growth especially in the case of the use of super accumulators.
Metals can be recovered from plants in special facilities (phytomining).	Requires constant monitoring and beyond the end of completion of phytoremediation process the end of integration.
Enriches the soil with organic ingredients and microorganisms, improving soil quality.	Climatic or hydrological conditions may limit the rate of plant growth.
Protection of the soil from erosion and runoff that can be caused by wind and water.	The fate of metals in plant biomass is a matter of concern. Risk of introduction into the food chain.
Can be combined with other mechanical technologies for better restoration results.	The contaminated area is not available for sale or rent and grazing. Problems in economic development

In addition, phytoremediation can be used in areas designated as unsuitable for cultivation, as a tool for soil and water protection and biodiversity enrichment. However, one of its major drawbacks is the very slow pace of recovery. The restoration of a contaminated area requires up to 10 years. The area under rehabilitation is no longer available for economic exploitation (e.g., sale, rent, grazing), which causes problems in the economic development of the region [65][68].

#### 2.5. Phytoaccumulation or Phytoextraction

Phytoaccumulation or phytoextraction is a green technology that uses plants and their associated microorganisms to reduce the concentration of inorganic chemicals in contaminated soil in situ, to such an extent that the treated soil can be reused for agricultural or any other purpose. It is based on the use of suitable plant species that pick up the pollutants from the roots and then transport and accumulate them in the aboveground parts, with the final result of harvesting and proper disposal of the contaminated plant material <sup>[74]</sup>

Phytoaccumulation is applied for the removal of metals such as Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, and Zn; metalloids such as As and Se; radionuclides such as 90Sr, 137Cs, 239Pu, 234U, and 238U; and non-metallic components such as B. It is not applicable in the case of the removal of organic pollutants or nutrients because their accumulation is prevented due to metabolic breakdown or evaporation. However, some studies have shown accumulation of native organic compounds in certain plants [77][78].

Higher plants respond to stress from heavy metals based on two strategies: (1) avoidance, according to which plants have mechanisms through which they exclude heavy metals from the environment; and (2) tolerance, when the metals accumulate and detoxify in plant tissue <sup>[47][79][80]</sup>. Avoidance is the most commonly used stress management strategy. By comparison, the accumulation of metals takes place in certain species of plants that grow mainly in mineral soils and are therefore characterized as metal accumulators or mineral plants <sup>[48][80]</sup>.

Brooks et al. <sup>[81]</sup> introduced the term hyperaccumulators to describe plants capable of accumulating more than 1000  $\mu$ g Ni g<sup>-1</sup> in their dry aboveground biomass <sup>[82][83]</sup>. However, some heavy metals (such as cadmium) are more toxic than nickel, so this criterion may not apply to all metals <sup>[83]</sup>. Consequently, hyperaccumulators are defined as plants that accumulate minerals in their tissues at concentrations 100 times higher than those measured in non-accumulating plants, without developing any symptoms of toxicity <sup>[84][85][86][87]</sup>. Given that the levels of cadmium in the aboveground parts of non-accumulators are usually <1 mg/kg, in order for a plant to be classified as an hyperaccumulator of cadmium it must have  $\geq$ 100 mg/kg <sup>[87]</sup>. Therefore, as a criterion for the characterization of a plant as a hyperaccumulator of a metal, the percentage of metal concentrated in the dry aboveground tissue was accepted <sup>[83]</sup>; in order for a plant to be classified as an hyperaccumulator it must have concentrations of more than 1000  $\mu$ g/g (0.1%) of Pb, Co, Cu, Cr and Ni, 10,000  $\mu$ g/g (1%) of Zn, and 100  $\mu$ g/g (0.01%) of Cd in its dry surface biomass <sup>[85][88][89]</sup>. It must also accumulate larger amounts of metal in its aboveground parts than in its roots so the ratio of concentrations of metals in the soil, accumulate metals in their roots <sup>[82][85][86][87][89][90]</sup>.

#### 2.6. Factors Influencing Phytoremediation Success

The effectiveness of phytoremediation is strongly influenced by factors related to soil properties and plant-specific characteristics. There have been many studies aiming to understand the specific qualities plants possess that render them able to withstand heavy metal exposure and even accumulate it in their tissues. Significantly, their innate ability to metabolically adapt in response to heavy metal stress (e.g., by controlling the expression rate of genes or the permeability of their membranes), makes certain genotypes better suited for phytoremediation applications <sup>[91]</sup>. In addition, there are some morphological characteristics that can advance phytoaccumulation of heavy metals; for instance, an extensive root system with good soil intrusion and large surface roots favors metal uptake <sup>[92]</sup>. The age of the plant also plays a role, as younger plants exposed to metal stress tend to be more severely affected. Even in the case of using plant cuttings, the larger the pieces used, the more successful the survival rate (e.g., in poplars and willows) <sup>[93][94][95][96]</sup>.

However, in addition to the proper selection of a plant species, the success of phytoextraction trials heavily depends on soil and environmental conditions in each case. Namely, the various factors affecting the solubility, mobility, and bioavailability of metals in soils also affect their uptake efficiency by plants <sup>[97]</sup>.

As heavy metals are positively charged, they are attracted to the negative charges of soil and sediment's colloids, and to cells, small particles, and humic substances, resulting in the formation of various complexes (usually inorganic). Complex formation and binding to macromolecules differs depending on the metal in question as the affinities for other elements are diversified. Interestingly, dicots have more negatively charged sites, located in the cell walls, than monocots <sup>[98]</sup>.

Soil pH, soil solution ionic strength, soil texture, organic matter and clay content, presence of Fe/Mn oxides, redox potential, and cation exchange capacity (CEC) are soil properties that play a major role in the aforementioned metal partitioning between liquid and solid phases, and their solubility and availability for plants <sup>[99][100][101][102][103][104][105][106]</sup> [107][108][109][110].

High soil CEC equals high root surface CEC, which means there is a higher possibility of binding of the metals to the negative charges. However, under low pH, the release of hydrogen cations causes high competition with the metals for binding spots on the colloids. Due to the higher affinity of H+, metals are subsequently released as they are being replaced, elevating the available fraction. The weathering of soil is also enhanced in acidic conditions <sup>[111]</sup>.

Soil texture is a key factor affecting the bioavailability of metals. In fact, higher levels of contaminants are commonly measured in fine-textured soils because they have a large specific surface area and a large charge (higher CEC), and therefore bind larger amounts of metals in comparison with coarse-textured soils <sup>[111]</sup>. Similarly, higher organic matter content serves as an immobilization component, binding the metals firmly and for longer time periods.

The soil conditions can significantly affect the phytoremediation process, which also impacts the soils' physical properties <sup>[112]</sup>. Hajabbasi <sup>[113]</sup> note that a soil for phytoremediation should have properties (physical, chemical, and biological) that enhance plant growth rates as much as possible, by providing favorable environments for the established plants to develop and sustain high microbial activity. The remediation process is highly dependent on the soil–organisms–plant interactions <sup>[114]</sup>, and thus on the soil's physical properties, such as texture, structural status, aeration, water conductivity, compaction, saturated hydraulic conductivity, and penetration resistance <sup>[115]</sup>, and also on the soil's microenvironment (temperature, moisture, heat exchange). To preserve high remediation rates in many cases, it is suggested to improve the soils' physical properties, and/or the phytostabilization or the phytoextraction capacities. Miranda et al. <sup>[116]</sup> suggest that the use of sheep manure, gypsum, and polymer can increase saturated hydraulic conductivity and macroporosity in the superficial layer but reduce soil penetration resistance. To assist phytoremediation, Acuña et al. <sup>[117]</sup> found that chelating agents can increase microaggregate stability, but stated that the addition of fulvic acids decreases the available soil water when applied to lead-contaminated soils.

Soil salinity is a constricting value in phytoremediation as plants are water stressed and display very low uptake rates due to osmotic imbalance <sup>[93]</sup>.

Soil temperature, in addition to atmospheric temperature and light, indirectly affect metal uptake by having an impact on plant growth <sup>[93]</sup>. The soil–plant interactions are complex and the soil properties should be acknowledged as a significant factor that must be carefully considered before the application of phytoremediation methods to contaminated soils.

Climate conditions can significantly affect metal contaminants' availability in soil and the absorption rates of the plants. In the Mediterranean climate, the adverse weather conditions impact plants' growth <sup>[118]</sup>, and therefore affect the

phytoextraction rates of trace elements from contaminated soils  $\frac{[119]}{120}$ . The Mediterranean climate conditions are generally characterized by hot, dry summers and seasonally restricted rainfall  $\frac{[120][121]}{120}$ , and have presented increasing aridity during recent decades compared to the past  $\frac{[122]}{122}$ . The particular regional climate characteristics  $\frac{[123]}{124}$  induce spatial and temporal variability in photosynthetic rates, and especially for plants used in phytoextraction  $\frac{[124]}{124}$ . Thus, plants using C<sub>4</sub> photosynthesis are more adapted compared to C<sub>3</sub> plants to the hot and dry Mediterranean environments, and can better cope with the frequent droughts occurring in the Mediterranean region. Those differences introduced by climate and weather conditions (mainly concerning temperature and water availability) can impact plants' ability to absorb metals from contaminated soils. Thus, plants used in phytoremediation should have stress tolerance to seasonal drought and heat, which are characteristics of the Mediterranean environment  $\frac{[125]}{20}$ .

Furthermore, the rhizosphere's microbiome has been shown to affect the availability of metals and their uptake by plants. Plant-microbe-induced solubilization constitutes the most prominent means in which the microbial community assists metal uptake. Exudates of both plants and microbes in the rhizosphere act as metal-chelating agents (e.g., phytosiderophores, organic acids), facilitating the mobility and availability of heavy metals <sup>[93][97]</sup>.

Finally, phytoremediation projects should aim at the extraction of a specific metal, in order to avoid interaction and competition with other metals present in the soil, which may hinder the essential purpose of the project <sup>[97]</sup>.

# 3. Plants and Phytoremediation

# 3.1. Plant Selection Criteria for an Effective Phytoremediation

When plants are to be selected for a successful phytoremediation, certain criteria must be considered. The most important selection criterion is a high biomass production, which will provide high levels of metal ion removal <sup>[126]</sup>. Other criteria are: the levels of tolerance concerning the specific metal existing at the site; root characteristics and depth of the root zone; medium properties (agronomical practices enhancing phytoremediation, pH, addition of chelators, fertilizers, tolerance to water logging); and addition of chelating agent <sup>[127]</sup>. Having a good knowledge of these criteria is very important so that the overall performance by plant can be upgraded.

More than 582 plant species are able to accumulate environmental pollutants in approx. 0.2% of all angiosperms (trees, shrubs, grasses, and aquatic plants). Of these, 25% belong to the Brassicaceae family <sup>[128]</sup>. The ability to tolerate and hyperaccumulate is genetically inherited. Grasses, shrubs, and trees are equally preferred, due to their high growth rate, high adaptability to stress environments, and high biomass production. Good examples of plants having these qualities are Indian grass (*Sorghastrum nutans*) <sup>[129]</sup> and switchgrass (*Panicum virgatum*) <sup>[130]</sup>. Other crops such as *Thlaspi caerulescens, Ipomea alpine, Haumaniastrum robertii, Astragalus racemosus*, and *Sebertia acuminata* have very high bioaccumulation potential for Cd/Zn, Cu, Co, Se, and Ni, respectively <sup>[131]</sup>.

Plants responsible for Ni accumulation belong mostly to the Brassicaceae family and, specifically, to the genii *Thlaspi* and *Alyssum*. Plants belonging to the Crassulaceae family are used for Zn accumulation and other plants suitable for Se absorption are found in the Fabaceae, Asteraceae, Rubiaceae and Brassicaceae families. Finally, the Solanaceae present a number of Cd hyperaccumulators <sup>[2][132]</sup>.

Regarding land decontamination, tree species can also be used. Some of these species are: willow (*Salix* sp.), poplar (*Populus* sp.), eucalyptus (*Eucalyptus* sp.), beech (*Fagus* sp.), maple (*Acer* sp.), birch (*Betula* sp.), spruce, pine, fir, larch, and hemlock, because of their fast growth rate and their capability to regrow. Willow and poplar are able to accumulate high concentration levels of Cd and Zn <sup>[133]</sup>. Some examples of important hyperaccumulators are presented in **Table 2**.

Table 2. Examples of plant species as hyper accumulators.

Heavy Metals	Plants	Bioaccumulation (mg or mg kg <sup>-1</sup> Dry Weight of Plant Tissue)
Cadmium (Cd)	Noccaea caerulescens	80 mg kg <sup>-1 [<u>134]</u></sup>
	Arabidopsis halleri	>100 μg kg <sup>−1</sup> [ <u>135]</u>
	Myriophyllum heterophyllum	21.46 μg kg <sup>-1 [<u>136</u>]</sup>
	Potamogeton crispus	49.09 μg g <sup>-1 [<u>136</u>]</sup>
	Atriplex halimus	57.66 mg kg <sup>-1 [<u>137]</u></sup>
	Helichrysum stoechas	5.89 mg kg <sup>-1 [<u>137]</u></sup>
	Ditrrichia viscosa	5.4 mg kg <sup>-1 [<u>137]</u></sup>
	Limonium cossonianum	3.94 mg kg <sup>-1 [<u>137]</u></sup>
	Piptatherum miliaceum	3.15 mg kg <sup>-1 [<u>137]</u></sup>
	Lygeum spartum	3.36 mg kg <sup>-1 [<u>137]</u></sup>
Nickel (Ni)	Alyssoides utriculata	>1000 mg kg <sup>-1</sup> (serpentine soils) $\frac{[138]}{}$
	Alyssones uncontra	39.7–366 mg kg <sup>-1</sup> (non-serpentine soils) <sup>[138]</sup>
	Brassica juncea	3916 mg kg <sup>-1 [<u>139</u>]</sup>
	Alyssum serpyllifolium subsp. Lusitanicum	38,105 mg kg <sup>-1 [139]</sup>
	Bromus hordeacus	1467 mg kg <sup>-1</sup> [ <u>140]</u>
	Linaria spartea	492 mg kg <sup>-1 [<u>140]</u></sup>
	Cupressus sempervirens	4.74 mg kg <sup>-1 [<u>141</u>]</sup>
	Eucalyptus citriodora	4.67 mg kg <sup>-1 [<u>141</u>]</sup>
	Pteris vittata	23,000 μg g <sup>-1 [<u>142]</u></sup>
Arsenic (As)	Pteris vittata	>1000 µg g <sup>−1</sup> [ <u>143]</u>
	Populus nigra	22,000 mg g <sup>-1 [<u>144]</u></sup>
	Zea mays	2538 mg kg <sup>-1</sup> [ <u>145</u> ]
Chromium (Cr)	Linaria spartea	707 mg kg−1 <sup>[<u>146]</u></sup>
	Phragmites australis	4825 mg kg <sup>-1 [<u>146</u>]</sup>
	Ulmus procera	173 mg kg <sup>-1 [<u>140]</u></sup>
Copper (Cu) Zinc (Zn)	Allysum serpyllifolium	130 mg kg <sup>-1 [<u>140]</u></sup>
	Brassica oleracea	8.34 mg kg <sup>-1 [<u>144]</u></sup>
	Eucalyptus camaldulensis	37.23 mg kg <sup>-1 [<u>141]</u></sup>
	Eucalyptus citriodora	36.16 mg kg <sup>-1 [<u>141]</u></sup>
	Brassica oleracea	381 mg kg <sup>-1 [<u>147]</u></sup>
	Sedum alfredii	13,799 mg kg <sup>-1 [<u>148]</u></sup>
	Noccaea caerulescens	19,410 mg kg <sup>-1 [<u>140]</u></sup>
	Matricaria chamomilla	271 mg kg <sup>-1 [<u>149][150]</u></sup>
	Verbascum phrygium	17,044.54 mg kg <sup>-1</sup> in roots <sup>[151]</sup>
	Eucalyptus camaldulensis	295.66 mg kg <sup>-1 [<u>141]</u></sup>
	Eucalyptus citriodora	299.37 mg kg <sup>-1 [<u>141]</u></sup>

Heavy Metals	Plants		Bioaccumulation (mg or mg kg <sup>-1</sup> Dry Weight of Plant Tissue)
Manganese (Mn)		Hibiscus sabdariffa	243 mg kg <sup>-1 [<u>152]</u></sup>
		Viotia neurophylla	>10,000 µg g <sup>-1 [<u>153]</u></sup>
		Eucalyptus camaldulensis	825.38 mg kg <sup>-1 [<u>142]</u></sup>
		Pinus halepensis	801.43 mg kg <sup>-1 [<u>147]</u></sup>
Uranium (U)		Helichrysum stoechas	4.91 mg kg <sup>-1 [<u>140]</u></sup>
		Hypochaeris radicata	4.07 mg kg <sup>-1 [<u>140]</u></sup>
Cobalt (Co)		Alyssum serpyllifolium	145 mg kg <sup>-1 [<u>140]</u></sup>
		Linaria spartea	63.2 mg kg <sup>-1</sup> [ <u>14][18]</u>
Lead (Pb)		Brassica junkea	112 mg g <sup>-1 [<u>144]</u></sup>
		Helianthuus annuus	60 mg g <sup>-1 [<u>144]</u></sup>
		Nicotiana tabacum	25 mg g <sup>-1 [<u>144]</u></sup>
		Cistus salvifolius	548 mg kg <sup>-1 [140]</sup>
		Lonicera periclymenum	318 mg kg <sup>-1 [<u>140]</u></sup>
		Eucalyptus camaldulensis	30.30 mg kg <sup>-1 [<u>141]</u></sup>

#### 3.2. Non-Native, Native, and Endemic Plant Species in the Phytoremediation

In certain cases, authors have suggested the use of non-native species due to the existence of physiological characteristics that allow them to grow under exceptional conditions. Even so, experience has shown that the use of alien plants can result in serious problems after their planting. Although non-native plants exhibit rapid growth and fast habituation, they can become invasive and their proliferation can cause extensive and unpredictable damage, leading to great cost. For example, *Eichomia crassipes* is a quite prolific accumulator of nickel (Ni), accumulating up to 6000 mg kg<sup>-1</sup> [<u>154</u>]. However, its services for phytoremediation cannot be exploited in the Mediterranean countries that are part of the European Union because, under Regulation No. 1143/2014, the breeding and transport of *E. crassipes* within the Union has been banned because of its invasive nature [<u>155</u>]. Moreover, two alien plant species (*Chromolaena odorata* and *Bidens pilosa*) are also recognized as hyperaccumulators for the phytoremediation of hazardous heavy metal i.e., cadmium. Therefore, there should be a thorough and integrated selection of plants suitable for phytoremediation that should stabilize the use of local seedbanks and native plant communities with phytoremediation goals [<u>156</u>].

Native plants demand less attention, are generally well-acclimatized, and, of course, do not present legal problems concerning their seed availability and transport. Mostly due to these reasons, scientists have increased their preliminary assessment of using native plant collection for phytostabilization in protected areas <sup>[156]</sup>. The possibility of preparing improvised blends of vegetation with phytoremediation properties creates a potential opening in the commercial market. However, because invasive species are already present or situated nearby, this project is dubious and perhaps disputable. The nature of the species itself poses a dilemma because there must be a choice between the prioritization of biodiversity management in a protected area and the application of ecological solutions regarding pollution <sup>[157]</sup>. A good example is the case of *Artiplex halimus*, a xerohalophyte with a high tolerance to metal and metalloid elements that is used as an ornamental plant, is potentially eligible for use in phytoremediation, and is associated with polluted sites in the National Park of Calanques in France. Nevertheless, results from this entry <sup>[157][158]</sup> showed that the potential for extensive dissemination of *A. halimus* by seed germination affects only the surrounding soils, which indicates that the maintenance of invasive populations may be a feasible option in order to discourage/prevent pollutant transfers.

The significance of endemic plant species regarding phytoremediation should also be noted, in addition to the importance of their conservation. As an area of significant biodiversity, the Mediterranean basin features 15,000–25,000 plant species, with the endemism percentage being as high as 60% <sup>[19]</sup>. An excellent example of an endemic bio-accumulators is *Alyssum serpyllifolium* subsp. *Lusitanicum*, which is an endemic plant that is widespread in Portugal <sup>[143]</sup> and is able to concentrate up to 38,105 mg Ni/kg DW in its aboveground tissues <sup>[140]</sup>. *Verbascum phrygium*, another example of an endemic bio-accumulator in the Mediterranean basin, only grows in parts of Asia Minor. It has been found to be a quite efficient bio-accumulator of zinc (Zn), with its roots able to withhold up to 17,044.54 mg kg<sup>-1</sup> DW <sup>[132]</sup>. However, due to

attributes such as restricted distribution and population size, and the need for rather specific ecological and environmental conditions (with habitats being subjected to human-induced degradation), endemic plants are often faced with the danger of extinction, with raised awareness of the matter being noted in recent years [142][159].

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