

Review

# Agronomic Approaches for Characterization, Remediation, and Monitoring of Contaminated Sites

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**Abstract:** With a view to conserving or improving soil ecosystem services, environment-friendly techniques, such as bio- and phytoremediation, can effectively be used for the characterization, risk assessment, and remediation of contaminated agricultural sites. Polyannual vegetation (meadows, poplar, and cane stands) is widely considered the most efficient tool for remediation (extraction of bioavailable fraction of contaminants), for undertaking safety measures (reducing the mobility of contaminants towards other environmental compartments), and for restoring the ecosystem services of contaminated agricultural sites (biomass production, groundwater protection, C storage, landscape quality improvement, and cultural and educational services). The roles of agronomic approaches will be reviewed by focusing on the various steps in the whole remediation process: (i) detailed environmental characterization; (ii) phytoremediation for reducing risks for the environment and human health; (iii) agronomic management for improving efficiency of phytoremediation; and (iv) biomass recycling in the win-win perspective of the circular economy.

**Keywords:** phytoremediation; phytoextraction; phytostabilization; ecosystem services; safety measures; risk assessment; precision remediation

## 1. Introduction

Industrial and mining activities are the main sources of pollutants threatening human and ecosystem health [1], spreading potentially toxic elements (PTEs) and organic pollutants (mainly polycyclic aromatic hydrocarbons and dioxins) [2] in the environment. According to a recent report [2] from the European Commission (EC), there are estimated to be 2.5 million potentially contaminated sites. Of these sites, about 14% (340,000 sites) could be contaminated, and are likely to require remediation.

Current regulations for environmental characterization of agricultural sites are, in many countries, based on the total content of contaminants [3], even if the bioavailable and bioaccessible fractions represent the main risk for human health and the environment [4,5]. Above all, the contaminants dissolved in circulating soil solution are considered the most dangerous, in terms of transfer to the food chain or towards other environmental compartments [6–8].

Remediation techniques based on chemical and physical treatments can be efficient, but always entail high soil disturbance [9]. In addition, they can prove very expensive, amounting to an estimated annual cost of about 17.3 billion euros [10].

Phytoremediation is an inexpensive eco-friendly technique that uses plants and amendments to remediate contaminated soils, with the aim of reducing the risks for human health and for the environment [11], and restoring soil ecosystem services [12], such as nutrient cycling, biodiversity, and landscape.

Phytoremediation approaches can be classified according to the following mechanisms [13]:

1. Phytostabilization or phytoimmobilization: involves physical and chemical immobilization of metal contaminants by their sorption onto roots and fixation with different soil amendments. This technique includes the stabilization of soil particles, preventing bulk erosion and airborne transport to other environmental compartments.
2. Phytoextraction: plants extract metallic and organic compounds from soil to plant tissues.
3. Phytotransformation: non-microbial-mediated degradation of organic pollutants (phytodegradation) or contaminant volatilization through transpiration (phytovolatilization).
4. Phytostimulation or rhizodegradation: plants mineralize organic pollutants through enhanced microflora activity in the rhizosoil.
5. Phytofiltration: use of plant roots for reclamation of surface and groundwater and wastewater.

Assessment of contamination in agricultural land has to take into account the possible transfer of the bioavailable forms of contaminants from the soil to food crops, and the health risks for farmworkers, exposed to contaminated soil particles by ingestion, inhalation, and dermal contact.

This means that the main aims of remediation protocols of contaminated agricultural soils are (i) to perform a detailed assessment of risks; (ii) to phytoextract the bioavailable form of pollutants [4]; (iii) to avoid resuspension of contaminated soil particles [14]; (iv) to stimulate the biodegradation of organic contaminants; and (v) to preserve the productive function of such soils by producing non-food biomass for energy or green chemistry.

This review addresses the whole phytoremediation process, from detailed characterization to risk assessment and management (focusing on phytostabilization, phytoextraction, and rhizodegradation of bioavailable contaminants), using plants assisted by fertilization/biostimulation to improve soil fertility and its ecosystem services. Attention is paid to biomass production and development with environmentally-safe technologies in a circular economy perspective.

## 2. Environmental Characterization

Approaches to environmental characterization of potentially contaminated agricultural sites need to balance the need to quantify health and environmental risks with the cost effectiveness of this activity. The presence of hotspots with high levels of contamination may be inaccurately detected when a limited number of samples are collected, thus leading to under- or overestimation of environmental risk in large sites. In the former case, land use of the site is not appropriately changed, exposing people and the environment to risk; in the latter, sites with very highly contaminated hotspots can be classified as uniformly contaminated. This frequently leads to overspending due to the application of remediation techniques, even in non-contaminated sub-areas. That said, although higher resolution mapping allows precise identification of such hotspots, the high costs of collecting and analyzing large numbers of soil samples limit its application.

Langella et al. [15] highlighted the usefulness of preliminary indirect investigations by geophysical and spectrometric methods such as automatic resistivity profiling (ARP), multi-frequency electromagnetic (EM) conductivity meters (such as Profiler EMP-400 and DUAL-EM), and Gamma-ray and X-ray fluorescence. These measurements are aimed at mapping the spatial variability of both physical and chemical soil properties in order to identify the areas with a higher probability of contamination. Among these methods, Caporale et al. [16] proposed the X-ray fluorescence analyzer as a rapid, inexpensive, and accurate tool for assessing the variability of potentially toxic element (PTE) concentrations in soils. This approach reduces the costs of environmental characterization by concentrating the sample collection and analyses only in the sub-areas that are potentially contaminated.

Rocco et al. [5] proposed different analytical methods for assessing the bioavailability of PTEs on soil samples. Furthermore, Visconti et al. [17] suggested analyzing the composition of native vegetation to obtain information about the distribution, as well as the actual bioavailability, of the contaminants measured as the fraction stored in plant tissues.

Duri et al. [18,19] adopted a straightforward, inexpensive approach to evaluate the risk of contaminants entering the food chain. The authors proposed to cultivate leafy vegetables in the more contaminated hotspots to calculate the hazard quotient (ratio between the potential dietary exposure to a contaminant and the level at which no adverse effects are expected) of the different metal species.

Environmental characterization, based on the detailed distribution of contaminants, on their bioavailability, and hence the potential risks for the environment and human health, is therefore necessary to reduce the environmental and economic costs of remediation, in a perspective of more scientifically-based “precision remediation”.

### 3. Phytoremediation for Reducing or Eliminating Risks for the Environment and Human Health

As discussed above, phytoremediation consists of a pool of agricultural techniques aimed at reducing the concentration (i.e., rhizodegradation and phytoextraction) or the risk (i.e., phytostabilization) related to the presence of bioavailable contaminants in the soil by using plants [11,20].

Phytoextraction aims to accumulate bioavailable PTEs in crops, to concentrate them in easily-harvestable biomass to be disposed of or used in other industrial processes. The main PTE sinks are bark, culms, and leaves, and in some cases, also below-ground organs, such as roots and rhizomes [21].

Metal uptake can be significantly increased by selecting appropriate species and enhancing PTE transfer to plant tissues with specific cropping techniques. This process can significantly reduce the soil bioavailable PTE content, which represents the most hazardous fraction for the environment and human health. According to Alkorta et al. [22], the most suitable species for phytoextraction should have the following characteristics:

1. Tolerance to high PTE concentrations.
2. PTE accumulation in easily harvestable organs.
3. Fast-growing biomass.
4. High biomass accumulation.
5. High root growth.
6. Easy cropping management.
7. Genetically stable attributes.
8. Biomass useful for energy production or green chemistry.
9. Not appreciated by grazing animals.

Visconti et al. [23] proposed a preliminary analysis of native vegetation of contaminated sites and of their rhizosoils, for selecting the most suitable species for phytoextraction or phytostabilization on the basis of their bioconcentration and translocation factors. Short rotation forestry (SRF) crops fit perfectly with the above-mentioned attributes [24], proving to be appropriate tools for both reclaiming soils and producing large amounts of biomass [25,26]. Furthermore, perennial crop cultivation minimizes soil disturbance (no tillage), favoring C storage in the soil with the conversion of crop residues (e.g., litter) and root exudates into soil organic matter (SOM).

Among the tree species, the most suitable for phytoextraction are *Populus* spp. (poplar), *Eucalyptus* spp., and *Salix* spp. (willow), which have proved to be efficient PTE accumulators in contaminated areas in Central Europe [27]. High intraspecific variability suggests the importance of evaluating the affinity of different cultivars to the specific PTE to be remediated [28,29]. In order to increase the phytoremediation efficiency of the ecological structures, French et al. [30] proposed planting polyclonal stands, rather than monocultures of forest trees. This strategy can be adopted both to take advantage of the ability of specific clones to uptake PTEs, and to increase system resilience to other biotic and abiotic factors. This approach was supported by findings from Wang and Greger [31], which showed high variability in mercury tolerance and compartmentalization in plant tissues between different willow clones. Similar results were reported by Granel and colleagues [32] for willow grown on a multi-contaminated soil. The authors argued that clone selection can target phytoextraction or fodder

production storage, using plants with a preferential Cd allocation in above-ground or below-ground biomass, respectively.

Another tool consists of species belonging to the *Brassicaceae* family known for their high capacity to accumulate several PTEs in their tissues. *Brassica carinata* L. is also considered an interesting crop for accumulating PTEs in stems and leaves, also allowing interesting production of biofuel from oil seeds [33].

Finally, there are several polyannual herbaceous crops able to establish easily in contaminated soils, both for lignocellulosic biomass production, such as giant reed (*Arundo donax* L.), silvergrass (*Miscanthus giganteus* A.), switchgrass (*Panicum virgatum* L.), and canary reed grass (*Phalaris arundinacea* L.), and for biofuel production, such as castor bean (*Ricinus communis* L.). Giant reed showed interesting yields of lignocellulosic biomass from shoots under low fertility conditions [34], along with a preferential allocation of PTEs in rhizomes [21] suitable for harvest at the end of the phytoremediation program, with a significant removal of PTEs from the soil root layer. *Miscanthus* species are high-yielding, non-food perennial grasses considered a promising biomass crop for energy, bio-based products, and raw materials for various uses. *Miscanthus giganteus* can be used for phytomanagement of polluted sites, restoring ecosystem services [35] with a significant removal of PTEs in the harvestable aerial biomass [36,37]. Pogrzeba et al. [38] reported that *P. virgatum* may be considered a promising crop for reclamation and energy production in contaminated sites. As reported by Antonkiewicz and colleagues [36], both *Miscanthus giganteus* and *Phalaris arundinacea* (canary reed grass) can be very efficient in uptaking bioavailable PTEs from municipal sludge, meaning that phytoextraction systems including such crops can allow agronomic use of potentially toxic sludge, recycling nutrients and immobilizing PTEs in above-ground plant tissues. Castor bean also accumulates PTEs in lignocellulosic shoots, allowing an interesting production of oil seeds in arid conditions [39].

The above-mentioned herbaceous species, in addition to phytoextraction of PTEs, may be considered good candidates also for phytostabilization, thanks to the permanent soil covering. In Table 1, we provide a short list of species used for phytoextraction due to their ability to uptake PTEs in above-ground harvestable biomass.

**Table 1.** Tree and herbaceous crops suitable for phytoextraction.

Species	References
<i>Populus</i> spp.(poplar)	[26,27]
<i>Eucalyptus</i> spp.	[40,41]
<i>Salix</i> spp.(willow)	[27,31,32,42]
<i>Arundo donax</i> L. (giant reed)	[21,43]
<i>Brassica</i> spp.	[44,45]
<i>Ricinus communis</i> L. (castor bean)	[39]
<i>Miscanthus</i> spp.	[35–37]

Phytostabilization aims to break the exposure pathways to pollutants for people (i.e., common citizens and workers) frequenting a contaminated site. The main objective is to establish a self-sustaining vegetative cap for limiting leaching, stabilizing contaminants in the root zone, and reducing the risk of contaminated soil particle resuspension and spread towards the surrounding areas [14,46]. Such species have a greater capacity to uptake PTEs in the below-ground biomass (roots or rhizomes), while the transfer of heavy metals to the above-ground tissues is in some cases very limited.

Phytostabilization may be used to limit dust lifting which may be a contamination source in semi-arid and arid environments. In such cases, fast-growing species should be chosen, able to rapidly colonize the soil to form a compact turf for preventing wind erosion. Intercropping microthermal and macrothermal species allows soil to be rapidly covered during the wet–cold season with the former (e.g., ryegrass or fescue), and ensures high soil cover during the dry season with drought-resistant grass, such as Bermuda grass (*Cynodon dactylon* L.), dallisgrass (*Paspalum* spp.), or smilo grass (*Piptatherum miliaceum* L.) (Table 2).

The application of legume crops could be useful for increasing nutrient availability (i.e., N and P) for plants used in phytoremediation programs. Improvement in crop nutrient status may result in an increase in metal uptake as well as soil cover, thereby reducing the spreading of contaminants to air or groundwater; yet, the growth of legume crops and their efficiency in N enrichment of soil depends on the symbiosis with N-fixing bacteria. In contaminated soils, symbiotic bacteria have to be metal-tolerant, such as *Mesorhizobium metallidurans* or novel species of the genus *Rhizobium*, which were found to be associated with *Anthyllis vulneraria* in a Zn-contaminated soil [47]. In the nodules of the same species, Sujkowska-Rybkowska and colleagues [48] also found strains of *Bradyrhizobium* tolerant to Cd and Cu. Several metal-resistant strains of *Rhizobium* spp. and *Mesorhizobium* spp. tolerant to Ni, Co, and Cr were isolated from *Lotus corniculatus* nodules [49].

Nevertheless, the presence of legume crops in the vegetation cover of contaminated soils needs to be carefully considered in agricultural areas, since the possibility that contaminants can accumulate in shoots, and thence enter the food chain due to grazing, must be avoided.

In some cases, limiting access to polluted sites is mandatory to avoid grazing and food production. Castor bean proves effective in producing non-food or feed aerial biomass and accumulating PTEs in roots [50]. With the same purpose, other interesting species are perennial herbaceous fast-growing species, such as giant (*Arundo donax* L.) or common reed (*Miscanthus sinensis* L.), that are hypertolerant species able to grow on contaminated soils, creating a dense green barrier in a few years [43,51].

Many tree species reported for phytoextraction (Table 1) can lend a contribution to reducing ground wind speed and the consequent spread of contaminated soil particles towards surrounding areas [52], also providing aesthetic improvement of contaminated sites and economic benefits [30]. Some tree species, such as poplar, are known for their ability to transform soil contaminants to volatile compounds and spread them into the atmosphere through the transpiration flux. This remediation process is effective only with organic compounds and heavy metals such as Hg and Se [53,54].

Rhizodegradation is the main phytoremediation technique when organic compounds are the main soil contaminants. It is based on the ability of plants to modify and enhance the soil microflora through the release of root exudates and other compounds usable as a growth substrate by microorganisms. All agronomic practices aimed at increasing root growth and efficiency can positively affect rhizodegradation. In this context, organic fertilization and inoculation with endophytic bacteria and mycorrhizal fungi also play a major role, since they have been shown to reduce pollutant-induced stress [55]. In addition, rhizodegradation can also use massive inoculum of native bacteria, in order to increase the degradation of organic pollutants with the application of microbial formulations based on bacteria adapted to site-specific conditions [56].

**Table 2.** Grasses and herbaceous lignocellulosic crops for phytostabilization.

Species	References
<b>Lignocellulosic polyannual crop</b>	
<i>Miscanthus sinensis</i> A. (slivergrass)	[35–37]
<i>Phalaris arundinacea</i> L. (canary reed grass)	[36]
<i>Arundo donax</i> L. (giant reed)	[21]
<i>Phragmites australis</i> (Cav.) Trin. ex Steud. (common reed)	[57]
<i>Panicum virgatum</i> L. (switchgrass)	[38]
<b>Microthermal grasses</b>	
<i>Lolium perenne</i> L.	[58,59]
<i>Poa pratensis</i> L.	[58]
<i>Festuca</i> spp.	[60]
<i>Agrostis</i> spp.	
<i>Phleum pratense</i> L.	[61]
<i>Bromus inermis</i> Leiss.	
<i>Elymus</i> spp.	

Table 2. Cont.

Species	References
<b>Macrothermal grasses</b>	
<i>Paspalum</i> spp.	
<i>Cynodon dactylon</i> L. (Bermuda grass)	[62]
<i>Piptatherum iliaceum</i> L. (smilo grass)	[63,64]

#### 4. Agronomic Management for Improving Efficiency of Phytoextraction or Phytostabilization

The efficiency of phytoremediation can be enhanced through two agronomic techniques commonly employed in traditional crop management: fertilization with composted organic matter and inoculation with endophytic fungi [20]. The low fertility of soils, as often is the case of contaminated brownfield sites, and phytotoxicity due to high concentrations of contaminants require the addition of organic amendments (e.g., peat, compost, biochar, or animal manure) for reducing PTE mobility and allowing and/or improving plant growth [14,44,65].

Compost use in phytoremediation, with doses from 40 to 80 Mg ha<sup>-1</sup> (fresh weight), positively affects soil fertility, due to the improvement of (a) stability of soil structural aggregates; (b) biodegradation of organic contaminants; (c) activity of N-cycling bacteria; and (d) plant nutrient availability [20].

Amendment with humic substances affects PTE mobility and bioavailability, due to the formation of insoluble complexes that reduce passive PTE mobility (diffusion and mass transport) [66,67]. Nevertheless, they allow active PTE mobility (root uptake), thanks to the rhizosphere stimulation of PTE bioavailability [68].

Root-colonizing symbiotic microorganisms, such as arbuscular mycorrhizal fungi (AMF), are fairly common in the rhizosphere, and are able to establish a mutualistic symbiosis with plant roots [69] involving over 80% of vascular plants [70]. Arbuscular mycorrhizal fungi can enhance root uptake of PTEs and reduce phytotoxicity due to two different mechanisms: (i) dilution of PTE concentration in plant tissues for increased biomass growth [71]; and (ii) exclusion through precipitation or chelation in the rhizosphere, or their direct uptake in fungi tissues [72]. Zhang and colleagues [73] reported the ability of *Glomus mosseae* to reduce abiotic stresses due to PTEs in *Lolium perenne* L., thereby improving growth and photosynthesis. Promising results were also obtained by González-Chávez et al. [74], using *Acaulospora* spp. and *F. mosseae* BEG25 for assisted castor bean-based phytostabilization of a Pb-polluted battery recycling site.

Another option to enhance phytoremediation efficiency involves endophytic opportunistic fungi belonging to *Trichoderma* spp., which are characterized by rapid growth and low-specificity plant symbiosis [75]. Fungi belonging to this genus are well-known for the production of a large variety of depolymerizing enzymes [76] that can be useful for assisted phytoremediation. A widely used strain for this purpose is *T. harzianum* T22, which greatly increases the effectiveness of plants used for phytoremediation, as proved by experiments showing a significant decrease in soil metal content, due to inoculated fern and giant reed, and a significant increase in root biomass, compared to control plants [21]. An increase in PTE availability to plants resulting in higher PTE accumulation was also reported by Barea et al. [77] for inoculated pearl millet (*Pennisetum glaucum* L.) grown on a multi-metal (Cd, Cr, Cu, Fe, Na, and Zn) contaminated soil medium with tannery solid waste (TSW).

Endophytic bacteria are also reported for their efficiency in enhancing phytoextraction capacity, in improving bioremediation of organic contaminants, and reducing PTE phytotoxicity [78–81].

#### 5. Monitoring Phytoremediation

An appropriate monitoring plan should be scheduled in order to assess the effect of the adopted phytoremediation strategy. PTE phytoextraction can be quantified by assessing at each harvest the dry biomass and the PTE accumulation in each organ (i.e., leaves, branches, bark, culms, and rhizomes)

of the plant species concerned. The removal of PTEs (e.g., kg/ha or g/ha) can be calculated as the product of dry biomass multiplied by the PTE content, and then compared to soil bioavailable PTEs [5] measured in the root layer (0–30 cm and 30–60 cm depth) in order to assess the effects of crop uptake (e.g., SRF trees, grasses, and intercropped *Brassicaceae*) on PTE dynamics. Measurement of dynamics of organic pollutants in soil must be carried out when the phytoremediation strategy adopted is rhizo- or phytodegradation.

Another interesting approach has been proposed by Palladino and colleagues [82], who monitored the transpiration rate of poplar together with soil moisture in a Cd-contaminated site in order to estimate the reduction in PTE leaching due to root activity. This effect can be assessed by comparing the water balance in cropped soil with that in bare soil.

As discussed in Section 2, the effect of phytoremediation plans can also be assessed by evaluating the indirect risk of PTE transfer to the food chain [5]. To do so, PTE hyperaccumulator food crops (e.g., *brassicaceae* such as Indian mustard and rocket and *compositae* such as chicory) can be grown in hot spots with higher PTE content [18,19]. Thus, a comparison between PTE accumulation in food crops before and after a phytoextraction cycle provides significant information regarding the efficiency of the phytoremediation plan on PTE bioavailability.

In addition, the effect of the vegetative cap on soil particle dispersion can be monitored, in order to assess risk due to dust ingestion for people frequenting the site. This effect depends on the ability of selected grass species to produce compact turf (even during the dry season), as well as the windbreak effect of selected SRF species. Simple monitoring of dust lift can be carried out by setting specific samplers of particulate in the inter-row area. The most common samplers used for this purpose are Big Spring Number Eight or the Modified Wilson and Cook [83,84], and the PTE content of sampled air particulate can be compared to soil total PTE content to indirectly estimate the magnitude of dust lift.

## 6. Using Biomass in a Circular Economy Perspective

Large-scale application of phytoremediation is feasible only in the framework of an efficient energy production chain [85]. Biomass grown on low- and even moderately-contaminated soils do not usually pose any problem, their PTE content being below legal thresholds for thermal treatments. Nevertheless, the use of biomass grown on heavily polluted soils can be limited by the PTE content of such materials, posing the need to stabilize pollutants in easily-manageable byproducts or remove pollutants from biomass prior to energy conversion [86].

Energy production through direct combustion can be hazardous, due to the dispersion of PTEs with flying ashes, even if Chalot et al. [87] reported that fabric filters are effective at reducing their emissions in atmosphere below the legal limits. Pyrolysis is considered a viable option for the treatment of contaminated biomass, successfully tackling the challenges of metal pollutant risk control and volume reduction [88]. The process consists in the carbonization of biomaterials under specific temperatures, anoxic environments, and in hampering flame ignition [89]. The main outputs of this process are a solid byproduct, called char, pyrolytic oil, and syngas. Syngas can be converted using the Fischer–Tropsch process into a wide range of long carbon chain biofuels such as synthetic diesel, aviation fuel, or ethanol [90]. Biochar can also be used for energy production, even if it can be applied to cropland as a soil amendment to increase soil C stocks [91] and improve soil chemical and physical fertility, conferring several benefits upon crop growth and nutrient use efficiency [92].

Pyrolysis operating parameters may significantly affect the features of such products [93], and should aim to maximize PTE content in biochar when contaminated biomasses are used as feedstock. Indeed, high-temperature pyrolysis carried out under prolonged vapor residence time allows higher syngas yields [94] but poses serious risks due to PTE accumulation in oil and gaseous fractions. By contrast, slow pyrolysis has proved to be a safer technology for energy production since the regulation of maximum temperature and its rate of increase allows PTEs to be concentrated and immobilized in the solid fraction [95].

Another interesting technology for exploiting biomass consists in anaerobic digestion, a microbial-driven fermentation process of C sources to produce methane and a byproduct called digestate. The positive aspects of this process are the low cost of pretreatments, and the possibility of using feedstock with high water content [96]. In addition, the energy efficiency of methane derived from anaerobic digestion is comparable with that of biomass combustion or ethanol production [97]. Mudhoo and Kumar [98] reported a multi-faceted (stimulatory, inhibitory, or even toxic effect) response of the anaerobic digestion process to PTE content, depending on the metal species and their concentration in the biomass feedstock. In addition, another issue is represented by the PTE content in digestate, which could limit its possible application as soil amendment. A current opinion is that such biomass can also be pyrolyzed in order to recover energy and stabilize PTEs in biochar.

Leaching with deionized water can significantly improve the properties of biomass for thermal bioenergy conversion, leading to significant reduction in ashes, and hence in PTEs [99]. Nevertheless, the extraction of inorganic components is often associated with the removal of organics, causing a dry matter loss that reduces total energy and economic value of the biomass [100].

Furthermore, other traditional industrial products, such as paper, solid wood products, and reconstituted products (i.e., paper, chipboard, laminated beams, and extruded trim), can be considered for use of biomass grown on potentially-polluted sites, being currently considered environmentally safe [101,102].

## 7. Conclusions

The first step for maximizing the remediation efficiency of the contaminated sites is to acquire high spatial resolution information of site contamination. This would allow the intervention to be tailored to the specific problems of the different sub-areas within a perspective of precision remediation.

A further step is to acquire information about the bioavailability of contaminants, since this represents the main risk for the environment and human health. In this regard, an improvement in national regulations is required, since few countries (i.e., Germany, Austria, and Slovenia) currently have thresholds based on bioavailable forms of contaminants, rather than on total content.

The use of natural resources, such as annual plants or trees, allows the various site-specific problems to be tackled, thanks to the multiple roles that they can play in the contaminated ecosystems:

- (1) Phytoextraction for remediating the soil by gradually reducing the bioavailable fraction of PTEs that will be accumulated in harvestable biomass.
- (2) Phytostabilization for interrupting the exposure pathways of contaminants, thus making the site safe by reducing their mobility towards air and groundwater.
- (3) Rhizodegradation for stimulating the biodegradation of organic contaminants by soil microflora.
- (4) Environmental restoration for recovering ecosystem services such as biodiversity, groundwater protection, C storage in soil, and landscape quality.

When more than one of the above objectives is desirable, the simultaneous use of different techniques is also possible, such as growing trees (poplar, eucalyptus, and willow) intercropped with microthermal/macrothermal grasses and amended with organic fertilizers, in order to combine the phytoextractive ability of trees with the effect of turf in preventing lifting and dispersion of soil particles. In hotspot areas with very high contaminant levels, it is possible to opt for permanent vegetative capping with dense stands of common reed or giant reed that prove effective at interrupting contaminant exposure pathways, limiting the leaching of contaminants towards the groundwater and immobilizing them in below-ground organs and in the upper soil layers. A large number of microbiological tools involving endophytic fungi or bacteria, as well as mycorrhiza, can be used to assist phytoremediation by increasing contaminant tolerance, thus increasing crop growth and metal uptake, as well as enhancing rhizodegradation of organic pollutants. This approach can be coupled with organic fertilization with composted biomass in order to allow a reduction in passive mobility of inorganic pollutants, as well as enhancement of chemical and physical fertility of contaminated soils.



Finally, various environmentally-safe technologies have been studied for converting biomass into renewable energy or materials, thereby improving the economic and environmental efficiency of the remediation process within a circular economy perspective.

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## References

1. Pogrzeba, M.; Krzyżak, J.; Rusinowski, S.; McCalmont, J.; Jensen, E. Energy Crop at Heavy Metal-Contaminated Arable Land as an Alternative for Food and Feed Production: Biomass Quantity and Quality. In *Plant Metallomics and Functional Omics A System-Wide Perspective*; Gaurav, S., Ed.; Springer Nature: Cham, Switzerland, 2019; pp. 1–21. [[CrossRef](#)]
2. Van Liedekerke, M.; Prokop, G.; Rabl-Berger, S.; Kibblewhite, M.; Louwagie, G. *Progress in the Management of Contaminated Sites in Europe*; European Commission, Joint Research Centre: Ispra, Italy; Publications Office of the European Union: Luxembourg, 2014; p. 72. [[CrossRef](#)]
3. Carlon, C.; D’Alessandro, M.; Swartjes, F. *Derivation Methods of Soil Screening Values in Europe. A Review and Evaluation of National Procedures towards Harmonization*; Carlon, C., Ed.; European Commission, Joint Research Centre: Ispra, Italy, 2007; 306p.
4. Agrelli, D.; Caporale, A.G.; Adamo, P. Assessment of bioavailability and speciation of heavy metal(loid)s and hydrocarbons for risk-based soil remediation. *Agronomy* **2020**. under review.
5. Rocco, C.; Agrelli, D.; Tafuro, M.; Caporale, A.G.; Adamo, P. Assessing the bioavailability of potentially toxic elements in soil: A proposed approach. *Ital. J. Agron.* **2018**, *13*, 16–22. [[CrossRef](#)]
6. Harmsen, J. Measuring bioavailability: From a scientific approach to standard methods. *J. Environ. Qual.* **2015**, *36*, 1420–1428. [[CrossRef](#)]
7. Adamo, P.; Zampella, M. Chemical speciation to assess bioavailability, bioaccessibility and geochemical forms of potentially toxic metals (PTMs) in polluted soils. In *Environmental Geochemistry, Site Characterization, Data Analysis and Case Histories*; De Vivo, B., Belkin, H.E., Lima, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; pp. 153–194. [[CrossRef](#)]
8. Harmsen, J.; Naidu, R. Bioavailability as a tool in site management. *J. Hazard. Mater.* **2013**, *261*, 840–846. [[CrossRef](#)] [[PubMed](#)]
9. Gil-Diaz, M.; Gonzalez, A.; Alonso, J.; Lobo, M.C. Evaluation of the stability of a nanoremediation strategy using barley plants. *J. Environ. Manag.* **2016**, *165*, 150–158. [[CrossRef](#)] [[PubMed](#)]
10. EC (European Commission). *Impact Assessment of the Thematic Strategy on Soil Protection*; Commission Staff Working Document; EC (European Commission): Brussels, Belgium, 2006; SEC (2006)620 22.9.2006.
11. Ali, H.; Khan, E.; Sajad, M.A. Phytoremediation of heavy metals—Concepts and applications. *Chemosphere* **2013**, *91*, 869–881. [[CrossRef](#)] [[PubMed](#)]
12. Vangronsveld, J.; Herzig, R.; Weyens, N.; Boulet, J.; Adriaensen, K.; Ruttens, A.; Thewys, T.; Vassilev, A.; Meers, E.; Nehnevajova, E.; et al. Phytoremediation of contaminated soils and groundwater: Lessons from the field. *Environ. Sci. Pollut. Res.* **2009**, *16*, 765–794. [[CrossRef](#)]
13. Ashraf, S.; Ali, Q.; Zahir, Z.A.; Ashraf, S.; Asghar, H.N. Phytoremediation: Environmentally sustainable way for reclamation of heavy metal polluted soils. *Ecotoxicol. Environ. Safe.* **2019**, *174*, 714–727. [[CrossRef](#)]
14. Visconti, D.; Álvarez-Robles, M.J.; Fiorentino, N.; Fagnano, M.; Clemente, R. Use of *Brassica juncea* and *Dactylis glomerata* for the phytostabilization of mine soils amended with compost or biochar. *Chemosphere* **2020**, *260*, 127661. [[CrossRef](#)]

15. Langella, G.; Agrillo, A.; Basile, A.; De Mascellis, R.; Manna, P.; Moretti, P.; Mileti, F.A.; Terribile, F.; Vingiani, S. Geography of soil contamination for characterization and precision remediation of potentially contaminated sites. *Ital. J. Agron.* **2018**, *13*, 6–15. [[CrossRef](#)]
16. Caporale, A.G.; Adamo, P.; Capozzi, F.; Langella, G.; Terribile, F.; Vingiani, S. Monitoring metal pollution in soils using portable-XRF and conventional laboratory-based techniques: Evaluation of the performance and limitations according to metal properties and sources. *Sci. Total Environ.* **2018**, *643*, 516–526. [[CrossRef](#)] [[PubMed](#)]
17. Visconti, D.; Fiorentino, N.; Stinca, A.; Di Mola, I.; Fagnano, M. Use of the native vascular flora for risk assessment and management of an industrial contaminated soil. *Ital. J. Agron.* **2018**, *13*, 23–33.
18. Duri, L.G.; Fiorentino, N.; Cozzolino, E.; Ottaiano, L.; Agrelli, D.; Fagnano, M. Bioassays for evaluation of sanitary risks from food crops cultivated in potentially contaminated sites. *Ital. J. Agron.* **2018**, *13*, 45–52. [[CrossRef](#)]
19. Duri, L.G.; Visconti, D.; Fiorentino, N.; Adamo, P.; Fagnano, M.; Caporale, A.G. Health Risk Assessment in Agricultural Soil Potentially Contaminated by Geogenic Thallium: Influence of Plant Species on Metal Mobility in Soil-Plant System. *Agronomy* **2020**, *10*, 890. [[CrossRef](#)]
20. Fiorentino, N.; Mori, M.; Cenvinzo, V.; Duri, L.G.; Gioia, L.; Visconti, D.; Fagnano, M. Assisted phytoremediation for restoring soil fertility in contaminated and degraded land. *Ital. J. Agron.* **2018**, *13*, 34–44. [[CrossRef](#)]
21. Fiorentino, N.; Fagnano, M.; Adamo, P.; Impagliazzo, A.; Mori, M.; Pepe, O.; Ventorino, V.; Zoina, A. Assisted phytoextraction of heavy metals: Compost and Trichoderma effects on giant reed uptake and soil quality. *Ital. J. Agron.* **2013**, *8*, 244–254. [[CrossRef](#)]
22. Alkorta, I.; Hernandez-Allica, J.; Becerril, J.M.; Amezaga, I.; Albizu, I.; Garbisu, C. Recent findings on the phytoremediation of soils contaminated with environmentally toxic heavy metals and metalloids such as zinc, cadmium, lead and arsenic. *Rev. Environ. Health* **2004**, *3*, 71–90. [[CrossRef](#)]
23. Visconti, D.; Fiorentino, N.; Caporale, A.G.; Stinca, A.; Adamo, P.; Motti, R.; Fagnano, M. Analysis of native vegetation for detailed characterization of a soil contaminated by tannery waste. *Environ. Pollut.* **2019**, *252*, 1599–1608. [[CrossRef](#)]
24. Rockwood, D.L.; Naidu, C.V.; Carter, D.R.; Rahmani, M.; Spriggs, T.A.; Lin, C.; Alker, G.R.; Isebrands, J.G.; Segrest, S.A. Short-rotation woody crops and phytoremediation, Opportunities for agroforestry? *Agrofor. Syst.* **2004**, *61*, 51–63. [[CrossRef](#)]
25. Pulford, I.D.; Watson, C. Phytoremediation of heavy metal-contaminated land by trees—A review. *Environ. Int.* **2003**, *29*, 529–540. [[CrossRef](#)]
26. Capuana, M. Heavy metals and woody plants—Biotechnologies for phytoremediation. *iFor. Biogeosci. For.* **2011**, *4*, 7–15. [[CrossRef](#)]
27. Unterbrunner, R.; Puschenreiter, M.; Sommer, P.; Wieshammer, G.; Tlustos, P.; Zupan, M.; Wenzel, W.W. Heavy metal accumulation in trees growing on contaminated sites in Central Europe. *Environ. Pollut.* **2007**, *148*, 107–114. [[CrossRef](#)] [[PubMed](#)]
28. Watson, C.; Pulford, I.D.; Riddell-Black, D. Screening of willow species for resistance to heavy metals, comparison of performance in a hydroponics system and field trials. *Int. J. Phytoremed.* **2003**, *5*, 351–365. [[CrossRef](#)] [[PubMed](#)]
29. Laureysens, I.; Blust, R.; De Temmerman, L.; Lemmens, C.; Ceulemans, R. Clonal variation in heavy metal accumulation and biomass production in a poplar coppice culture. II. Seasonal variation in leaf, wood and bark concentrations. *Environ. Pollut.* **2004**, *131*, 485–494. [[CrossRef](#)] [[PubMed](#)]
30. French, C.J.; Dickinson, N.M.; Putwain, P.D. Woody biomass phytoremediation of contaminated brownfield land. *Environ. Pollut.* **2006**, *141*, 387–395. [[CrossRef](#)]
31. Wang, Y.; Greger, M. Clonal differences in mercury tolerance, accumulation, and distribution in willow. *J. Environ. Qual.* **2004**, *33*, 1779–1785. [[CrossRef](#)] [[PubMed](#)]
32. Granel, T.; Robinson, B.H.; Mills, T.M.; Clothier, B.E.; Green, S.R.; Fung, L. Cadmium accumulation by willow clones used for conservation, stock fodder and phytoremediation. *Aust. J. Soil Res.* **2002**, *40*, 1331–1337. [[CrossRef](#)]
33. Cardone, M.; Mazzoncini, M.; Menini, S.; Rocco, V.; Senatore, A.; Seggiani, M.; Vitolo, S. *Brassica carinata* as an alternative oil crop for the production of biodiesel in Italy: Agronomic evaluation, fuel production by transesterification and characterization. *Biomass Bioenergy* **2003**, *25*, 623–636. [[CrossRef](#)]

34. Fagnano, M.; Impagliazzo, A.; Mori, M.; Fiorentino, N. Agronomic and Environmental Impacts of Giant Reed (*Arundo donax* L.): Results from a Long-Term Field Experiment in Hilly Areas Subject to Soil Erosion. *Bioenergy Res.* **2015**, *8*, 415–422. [[CrossRef](#)]
35. Nsanganwimana, F.; Pourrut, B.; Mench, M.; Douay, F. Suitability of *Miscanthus* species for managing inorganic and organic contaminated land and restoring ecosystem services. A review. *J. Environ. Manag.* **2014**, *143*, 123–134. [[CrossRef](#)]
36. Antonkiewicz, J.; Kolodziej, B.; Bielinska, E.J. The use of reed canary grass and giant miscanthus in the phytoremediation of municipal sewage sludge. *Environ. Sci. Pollut. Res.* **2016**, *23*, 9505–9517. [[CrossRef](#)] [[PubMed](#)]
37. Pogrzeba, M.; Rusinowski, S.; Sitko, K.; Krzyżak, J.; Skalska, A.; Małkowski, E.; Ciszek, D.; Werle, S.; Mc Calmont, J.P.; Mos, M.; et al. Relationships between soil parameters and physiological status of *Miscanthus x giganteus* cultivated on soil contaminated with trace elements under NPK fertilisation vs. microbial inoculation. *Environ. Pollut.* **2017**, *225*, 163–174. [[CrossRef](#)] [[PubMed](#)]
38. Pogrzeba, M.; Rusinowski, S.; Krzyżak, J. Macroelements and heavy metals content in *Panicum virgatum* cultivated on contaminated soil under different fertilization. *Int. J. Agric. For.* **2017**, *63*, 69–76. [[CrossRef](#)]
39. Roychowdhury, R.; Roy, M.; Zaman, S.; Mitra, A. Phytoremediation potential of castor oil plant (*Ricinus communis*) grown on fly ash amended soil towards lead bioaccumulation. *Innov. Food Sci. Emerg. Technol.* **2019**, *6*, 156–160.
40. Luo, J.; Qi, S.; Peng, L.; Wang, J. Phytoremediation efficiency of Cd by *Eucalyptus globulus* transplanted from polluted and unpolluted sites. *Int. J. Phytoremed.* **2016**, *18*, 308–314. [[CrossRef](#)]
41. Arriagada, C.; Pereira, G.; García-Romera, I.; Ocampo, J.A. Improved zinc tolerance in *Eucalyptus globulus* inoculated with *Glomus deserticola* and *Trametes versicolor* or *Corioloopsis rigida*. *Soil Biol. Biochem.* **2010**, *42*, 118–124. [[CrossRef](#)]
42. Lewandowski, I.; Schmidt, U.; Londo, M.; Faaij, A. The economic value of the phytoremediation function—Assessed by the example of cadmium remediation by willow (*Salix* ssp). *Agric. Sys.* **2006**, *89*, 68–89. [[CrossRef](#)]
43. Barbosa, B.; Boléo, S.; Sidella, S.; Costa, J.; Duarte, M.P.; Mendes, B.; Cosentino, S.L.; Fernando, A.L. Phytoremediation of heavy metal-contaminated soils using the perennial energy crops *Miscanthus* spp. and *Arundo donax* L. *BioEnergy Res.* **2015**, *8*, 1500–1511. [[CrossRef](#)]
44. Clemente, R.; Walker, D.J.; Bernal, M.P. Uptake of heavy metals and As by *Brassica juncea* grown in a contaminated soil in Aznalcollar (Spain): The effect of soil amendments. *Environ. Pollut.* **2005**, *138*, 46–58. [[CrossRef](#)]
45. Marchiol, L.; Sacco, P.; Assolari, S.; Zerbi, G. Reclamation of polluted soil: Phytoremediation potential of crop-related *Brassica* species. *Water Air Soil Pollut.* **2004**, *158*, 345–356. [[CrossRef](#)]
46. Pardo, T.; Martínez-Fernández, D.; Clemente, R.; Bernal, M.P.; Walker, D.J. The use of olive-mill waste compost to promote the plant vegetation cover in a trace element-contaminated soil. *Environ. Sci. Pollut. Res.* **2014**, *21*, 1029–1038. [[CrossRef](#)] [[PubMed](#)]
47. Grison, C.M.; Jackson, S.; Merlot, S.; Dobson, A.; Grison, C. *Rhizobium metallidurans* sp. nov., a symbiotic heavy metal resistant bacterium isolated from the *Anthyllis vulneraria* Zn-hyperaccumulator. *Int. J. Syst. Evol. Microbiol.* **2015**, *65*, 1525–1530. [[CrossRef](#)] [[PubMed](#)]
48. Sujkowska-Rybkowska, M.; Wazny, R. Metal resistant rhizobia and ultrastructure of *Anthyllis vulneraria* nodules from zinc and lead contaminated tailing in Poland. *Int. J. Phytoremed.* **2018**, *20*, 709–720. [[CrossRef](#)] [[PubMed](#)]
49. Sujkowska-Rybkowska, M.; Kasowska, D.; Gediga, K.; Banasiewicz, J.; Stępkowski, T. *Lotus corniculatus*-rhizobia symbiosis under Ni, Co and Cr stress on ultramafic soil. *Plant Soil* **2020**, *451*, 459–484. [[CrossRef](#)]
50. Ruiz Olivares, A.; Carrillo-González, R.; González-Chávez, M.C.; Soto Hernández, R.M. Potential of castor bean (*Ricinus communis* L.) for phytoremediation of mine tailings and oil production. *J. Environ. Manag.* **2013**, *114*, 316–323. [[CrossRef](#)]
51. Fiorentino, N.; Ventorino, V.; Rocco, C.; Cenvinzo, V.; Agrelli, D.; Gioia, L.; Di Mola, I.; Adamo, P.; Fagnano, M. Giant reed growth and effects on soil biological fertility in assisted phytoremediation of an industrial polluted soil. *Sci. Total Environ.* **2017**, *575*, 1375–1383. [[CrossRef](#)]

52. Schnoor, J.L. Phytostabilization of metals using hybrid poplar trees. In *Phytoremediation of Toxic Metals, Using Plants to Clean Up the Environment*; Raskin, I., Ensley, B.D., Eds.; John Wiley: New York, NY, USA, 2000; pp. 133–150. [[CrossRef](#)]
53. Padmavathiamma, P.K.; Li, L.Y. Phytoremediation technology: Hyperaccumulation metals in plants. *Water Air Soil Pollut.* **2017**, *184*, 105–126. [[CrossRef](#)]
54. Kumar, V.; Shahi, S.K.; Singh, S. Bioremediation: An eco-sustainable approach for restoration of contaminated sites. In *Microbial Bioprospecting for Sustainable Development*; Singh, J., Sharma, D., Kumar, G., Sharma, N.R., Eds.; Springer: Singapore, 2018; pp. 115–136. [[CrossRef](#)]
55. Shim, H.; Chauhan, S.; Ryoo, D.; Bowers, K.; Thomas, S.M.; Canada, K.A.; Burken, J.L.; Wood, T.K. Rhizosphere competitiveness of trichloroethylene-degrading, poplar-colonizing recombinant bacteria. *Appl. Environ. Microbiol.* **2000**, *66*, 4673–4678. [[CrossRef](#)]
56. Abhilash, P.C.; Powell, J.R.; Singh, H.B.; Singh, B.K. Plant microbe interactions: Novel applications for exploitation in multipurpose remediation technologies. *Trends Biotechnol.* **2012**, *30*, 416–420. [[CrossRef](#)]
57. De Giudici, G.; Pusceddu, C.; Medas, D.; Meneghini, C.; Gianoncelli, A.; Rimondi, V.; Podda, F.; Cidu, R.; Lattanzi, P.; Wanty, R.B.; et al. The role of natural biogeochemical barriers in limiting metal loading to a stream affected by mine drainage. *Appl. Geochem.* **2017**, *76*, 124–135. [[CrossRef](#)]
58. Padmavathiamma, P.; Li, L. Effect of Amendments on phytoavailability and fractionation of copper and zinc in a contaminated soil. *Int. J. Phytoremed.* **2010**, *12*, 697–715. [[CrossRef](#)] [[PubMed](#)]
59. Karami, N.; Clemente, R.; Moreno-Jiménez, E.; Lepp, N.W.; Beesley, L. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. *J. Hazard. Mater.* **2011**, *191*, 41–48. [[CrossRef](#)] [[PubMed](#)]
60. Cuske, M.; Karczewska, A.; Gałka, B.; Dradrach, A. Some adverse effects of soil amendment with organic materials—The case of soils polluted by copper industry phytostabilized with red fescue. *Int. J. Phytoremed.* **2016**, *18*, 839–846. [[CrossRef](#)] [[PubMed](#)]
61. Mahar, A.; Wang, P.; Ali, A.; Awasthi, M.K.; Lahori, A.H.; Wang, Q.; Li, R.H.; Zhang, Z.Q. Challenges and opportunities in the phytoremediation of heavy metals contaminated soils: A review. *Ecotoxicol. Environ. Saf.* **2016**, *126*, 111–121. [[CrossRef](#)]
62. Shu, W.S.; Ye, Z.H.; Lan, C.Y.; Zhang, Z.Q.; Wong, M.H. Lead, zinc and copper accumulation and tolerance in populations of *Paspalum distichum* and *Cynodon dactylon*. *Environ. Pollut.* **2002**, *120*, 445–453. [[CrossRef](#)]
63. Garcia, G.; Faz, A.; Cunha, M. Performance of *Piptatherum miliaceum* (Smilo grass) in edaphic Pb and Zn phytoremediation over a short growth period. *Int. Biodeterior. Biodegrad.* **2004**, *54*, 245–250. [[CrossRef](#)]
64. Arco-Lázaro, E.; Martínez-Fernández, D.; Bernal, M.P.; Clemente, R. Response of *Piptatherum miliaceum* to co-culture with a legume species for the phytostabilisation of trace elements contaminated soils. *J. Soils Sediments* **2017**, *17*, 1349–1357. [[CrossRef](#)]
65. Kumpiene, J.; Lagerkvist, A.; Maurice, C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review. *Waste Manag.* **2008**, *28*, 215–225. [[CrossRef](#)]
66. Huang, M.; Zhu, Y.; Li, Z.; Huang, B.; Luo, N.; Liu, C.; Zeng, G. Compost as a soil amendment to remediate heavy metal-contaminated agricultural soil: Mechanisms, efficacy, problems, and strategies. *Water Air Soil Pollut.* **2016**, *227*, 1–18. [[CrossRef](#)]
67. Venegas, A.; Rigol, A.; Vidal, M. Viability of organic wastes and biochars as amendments for the remediation of heavy metal-contaminated soils. *Chemosphere* **2015**, *119*, 190–198. [[CrossRef](#)]
68. Halim, M.; Conte, P.; Piccolo, A. Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. *Chemosphere* **2003**, *52*, 265–275. [[CrossRef](#)]
69. Todeschini, V.; Franchin, C.; Castiglione, S.; Burlando, B.; Biondi, S.; Torrigiani, P. Responses of two registered poplar clones to copper, after inoculation, or not, with arbuscular mycorrhizal fungi. *Caryologia* **2007**, *60*, 146–155. [[CrossRef](#)]
70. Berruti, A.; Lumini, E.; Balestrini, R.; Bianciotto, V. Arbuscular mycorrhizal fungi as natural biofertilizers: Let's benefit from past successes. *Front. Microbiol.* **2016**, *6*, 1559. [[CrossRef](#)] [[PubMed](#)]
71. Kaldorf, M.; Kuhn, A.J.; Schröder, W.R.; Hildebrandt, U.; Bothe, H. Selective element deposits in maize colonized by a heavy metal tolerance conferring arbuscular mycorrhizal fungus. *J. Plant Physiol.* **1999**, *154*, 718–728. [[CrossRef](#)]
72. Christie, P.; Li, X.; Chen, B. Arbuscular mycorrhiza can depress translocation of zinc to shoots of host plants in soils moderately polluted with zinc. *Plant Soil* **2004**, *261*, 209–217. [[CrossRef](#)]

73. Zhang, H.; Xu, N.; Li, X.; Long, J.; Sui, X.; Wu, Y.; Li, J.; Wang, J.; Zhong, H.; Sun, G.Y. Arbuscular mycorrhizal fungi (*Glomus mosseae*) improves growth, photosynthesis and protects photosystem II in leaves of *Lolium perenne* L. in cadmium contaminated soil. *Front. Plant Sci.* **2018**, *9*, 1156. [[CrossRef](#)]
74. González-Chávez, M.D.C.A.; Carrillo-González, R.; Cuellar-Sánchez, A.; Delgado-Alvarado, A.; Suárez-Espinosa, J.; Ríos-Leal, E.; Solís-Domínguez, F.A.; Maldonado-Mendoza, I.E. Phytoremediation assisted by mycorrhizal fungi of a Mexican defunct lead-acid battery recycling site. *Sci. Total Environ.* **2019**, *650*, 3134–3144. [[CrossRef](#)]
75. Zafar, S.; Aqil, F.; Ahmad, Q. Metal tolerance and biosorption potential of filamentous fungi isolated from metal contaminated agricultural soil. *Bioresour. Technol.* **2007**, *98*, 2557–2561. [[CrossRef](#)]
76. Ahamed, A.; Vermette, P. Culture-based strategies to enhance cellulase enzyme production from *Trichoderma reesei* RUT-C30 in bioreactor culture conditions. *Biochem. Eng. J.* **2008**, *40*, 399–407. [[CrossRef](#)]
77. Bareen, F.E.; Shafiq, M.; Jamil, S. Role of plant growth regulators and a saprobic fungus in enhancement of metal phytoextraction potential and stress alleviation in pearl millet. *J. Hazard. Mater.* **2012**, *237–238*, 186–193. [[CrossRef](#)]
78. Newman, L.A.; Reynolds, C.M. Bacteria and phytoremediation, new uses for endophytic bacteria in plants. *Trends Biotechnol.* **2005**, *23*, 6–8. [[CrossRef](#)] [[PubMed](#)]
79. Moore, F.P.; Barac, T.; Borremans, B.; Oeyen, L.; Vangronsveld, J.; van der Lelie, D.; Campbell, C.D.; Moore, E.R.B. Endophytic bacterial diversity in poplar trees growing on a BTEX-contaminated site, the characterisation of isolates with potential to enhance phytoremediation. *Syst. Appl. Microbiol.* **2006**, *29*, 539–556. [[CrossRef](#)] [[PubMed](#)]
80. Mastretta, C.; Taghavi, S.; van der Lelie, D.; Mengoni, A.; Galardi, F.; Gonnelli, C.; Barac, T.; Boulet, J.; Weyens, N.; Vangronsveld, J. Endophytic bacteria from seeds of *Nicotiana tabacum* can reduce cadmium phytotoxicity. *Int. J. Phytoremed.* **2009**, *11*, 251–267. [[CrossRef](#)]
81. Rajkumar, M.; Ae, N.; Freitas, H. Endophytic bacteria and their potential to enhance heavy metal phytoextraction. *Chemosphere* **2009**, *77*, 153–160. [[CrossRef](#)]
82. Palladino, M.; Nasta, P.; Capolupo, A.; Romano, N. Monitoring and modelling the role of phytoremediation to mitigate nonpoint source cadmium pollution and groundwater contamination at field scale. *Ital. J. Agron.* **2018**, *13*, 59–68. [[CrossRef](#)]
83. Gao, Y.; Dang, X.; Yu, Y.; Li, Y.; Liu, Y.; Wang, J. Effects of tillage methods on soil carbon and wind erosion. *Land Degrad. Dev.* **2016**, *27*, 583–591. [[CrossRef](#)]
84. Mendez, M.J.; Funk, R.; Buschiazzo, D.E. Efficiency of Big Spring Number Eight (BSNE) and Modified Wilson and Cook (MWAC) samplers to collect PM10, PM2.5 and PM1. *Aeolian Res.* **2016**, *21*, 37–44. [[CrossRef](#)]
85. Vigil, M.; Marey-Pérez, M.F.; Martínez Huerta, G.; Álvarez Cabal, V. Is phytoremediation without biomass valorization sustainable?—Comparative LCA of landfilling vs. anaerobic co-digestion. *Sci. Total Environ.* **2015**, *505*, 844–850. [[CrossRef](#)]
86. Gomes, H.I. Phytoremediation for bioenergy: Challenges and opportunities. *Environ. Technol. Rev.* **2012**, *1*, 59–66. [[CrossRef](#)]
87. Chalot, M.; Blaudez, D.; Rogaume, Y.; Provent, A.S.; Pascua, C. Fate of Trace Elements during the combustion of phytoremediation wood. *Environ. Sci. Technol.* **2012**, *46*, 13361–13369. [[CrossRef](#)]
88. Liu, Z.; Wang, L.; Xiao, H.; Guo, X.; Urbanovich, O.; Nagorskaya, L.; Li, X. A review on control factors of pyrolysis technology for plants containing heavy metals. *Ecotoxicol. Environ. Saf.* **2020**, *191*, 110181. [[CrossRef](#)] [[PubMed](#)]
89. Czernik, S.; Bridgwater, A.V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuel* **2004**, *18*, 590–598. [[CrossRef](#)]
90. Sims, R.E.; Mabee, W.; Saddler, J.N.; Taylor, M. An overview of second generation biofuel technologies. *Bioresour. Technol.* **2010**, *101*, 1570–1580. [[CrossRef](#)] [[PubMed](#)]
91. Kung, C.C.; Zhang, N. Renewable energy from pyrolysis using crops and agricultural residuals: An economic and environmental evaluation. *Energy* **2015**, *90*, 1532–1544. [[CrossRef](#)]
92. Fiorentino, N.; Sánchez-Monedero, M.A.; Lehmann, J.; Enders, A.; Fagnano, M.; Cayuela, M.L. Interactive priming of soil N transformations from combining biochar and urea inputs: A 15N isotope tracer study. *Soil Biol. Biochem.* **2019**, *131*, 166–175. [[CrossRef](#)]

93. Abbas, Q.; Liu, G.J.; Yousaf, B.; Ali, M.U.; Ullah, H.; Munir, M.A.M.; Liu, R.J. Contrasting effects of operating conditions and biomass particle size on bulk characteristics and surface chemistry of rice husk derived-biochars. *J. Anal. Appl. Pyrolysis* **2018**, *134*, 281–292. [[CrossRef](#)]
94. Chen, G.; Andries, J.; Luo, Z.; Spliethoff, H. Biomass pyrolysis/gasification for product gas production: The overall investigation of parametric effects. *Energy Convers. Manag.* **2003**, *44*, 1875–1884. [[CrossRef](#)]
95. Grottola, C.M.; Giudicianni, P.; Pindozi, S.; Stanzone, F.; Faugno, S.; Fagnano, M.; Fiorentino, N.; Ragucci, R. Steam assisted slow pyrolysis of contaminated biomasses: Effect of plant parts and process temperature on heavy metals fate. *Waste Manag.* **2019**, *85*, 232–241. [[CrossRef](#)]
96. Appels, L.; Lauwers, J.; Degève, J.; Helsen, L.; Lievens, B.; Willems, K.; Van Impe, J.; Dewil, R. Anaerobic digestion in global bio-energy production: Potential and research challenges. *Renew. Sustain. Energy Rev.* **2011**, *15*, 4295–4301. [[CrossRef](#)]
97. Parawira, W.; Read, J.S.; Mattiasson, B.; Björnsson, L. Energy production from agricultural residues: High methane yields in pilot-scale two-stage anaerobic digestion. *Biomass Bioenergy* **2008**, *32*, 44–50. [[CrossRef](#)]
98. Mudhoo, A.; Kumar, S. Effects of heavy metals as stress factors on anaerobic digestion processes and biogas production from biomass. *Int. J. Environ. Sci. Technol.* **2013**, *10*, 1383–1398. [[CrossRef](#)]
99. Wu, H.; Yip, K.; Kong, Z.; Li, C.-Z.; Liu, D.; Yu, Y.; Gao, X. Removal and Recycling of Inherent Inorganic Nutrient Species in Mallee Biomass and Derived Biochars by Water Leaching. *Ind. Eng. Chem. Res.* **2011**, *50*, 12143–12151. [[CrossRef](#)]
100. Yu, C.; Zheng, Y.; Cheng, Y.-S.; Jenkins, B.M.; Zhang, R.; Vander Gheynst, J.S. Solid–liquid extraction of alkali metals and organic compounds by leaching of food industry residues. *Bioresour. Technol.* **2010**, *101*, 4331–4336. [[CrossRef](#)] [[PubMed](#)]
101. Pandey, V.C.; Alonso, P.S. Market opportunities in sustainable phytoremediation. In *Phytomanagement of Polluted Sites*; Pandey, V.C., Baudh, K., Eds.; Elsevier Inc.: Amsterdam, The Netherlands, 2010; pp. 51–82. [[CrossRef](#)]
102. Licht, L.A.; Isebrands, J.G. Linking phytoremediated pollutant removal to biomass economic opportunities. *Biomass Bioenergy* **2005**, *28*, 203–218. [[CrossRef](#)]



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