

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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