



Agronomic Approaches for the Remediation of Contaminated Soils

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Contaminated soils can only be efficiently managed if proper procedures are adopted for evaluating the risks due to contamination as well as the actual volume of contaminated soil [1]. The environmental characterization of potentially contaminated sites is usually made by analyzing the total content of contaminants, while it is well-known that the bioavailable fraction of contaminants causes the major sanitary and environmental concerns. Furthermore, the sampling schemes adopted for the environmental characterization commonly include too few samples for a realistic assessment of the soil volume to be remediated, thus leading to under- or overestimation of environmental and sanitary risks [2].

Several approaches to overcoming these problems are reported in this Special Issue, including chemical methods for analyzing the bioavailability of contaminants [3] and bioassays for evaluating the risk of contaminant accumulation in food crops [4,5], which is strictly related to their bioavailability [6]. Geostatistical methods based on geophysical and spectrometric measures have also been proposed for the detailed mapping of soil spatial variability [7].

These methodologies should be considered by national legislations in order to enable a more efficient remediation.

Since the fundamental role of soil functions in ecosystem and economic stability is globally recognized, the prevention of further degradation, the preservation of soil functions, and the restoration of degraded soils are crucial, as stated by European Soil Thematic Strategy [8]. In this perspective, phytoremediation makes it possible to simultaneously reduce environmental and sanitary risks while preserving soil resources and ecosystem services (e.g., primary production, carbon storage, nutrient cycling, biodiversity, landscape quality) by different mechanisms [1]. In this Special Issue, the experimental results in phytoextraction [9,10], phytostabilization [11–13], and bio- phytodegradation [14,15] are presented.

Finally, phytoremediation coupled with the production of renewable energy is considered a winning strategy to avoid both sanitary and environmental risks due to soil contamination and land competition of biomass crops with food crops, in a circular economy perspective [16].

A detailed data spatialization is the basis for a precision remediation. Soil contamination is usually not homogeneous, as it is caused by negligent or intentional spilling of contaminated materials. This means that contaminated hotspots may not be appropriately detected by a low number of samples. On the other hand, high-resolution assessment in large areas is limited by the high costs of collecting and analyzing large numbers of soil samples.

Langella et al. [17] demonstrated the effectiveness of preliminary geophysical and spectrometric investigations by using automatic resistivity profiling (ARP), multi-frequency electromagnetic (EM) conductivity meters (e.g., Profiler EMP-400 and DUAL-EM), and gammaray and X-ray fluorescence. Among these methods, X-ray fluorescence analysis was particularly effective as a rapid, inexpensive, and accurate method for assessing the variability



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Copyright: © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). of potentially toxic element (PTE) concentrations in soils. The geospatial analysis of such data with a probabilistic approach makes it possible to define a detailed map of risks by estimating the probability of exceeding the threshold values of generic risk indicators [7]. These probability maps can be used for designing an appropriate sampling scheme, thus reducing the costs for soil collection and analysis.

Environmental characterization must consider risk assessment. In many countries, risk assessment is based on total concentrations as a first estimation of exposure, but more detailed information about the bioavailability of contaminants is considered necessary for an actual assessment of sanitary and environmental risks. Furthermore, assessing the bioavailability of contaminants is crucial for designing the most efficient phytoremediation strategy, since plants are able to uptake only the bioavailable forms of PTEs.

The bioavailability of potentially toxic elements is a dynamic concept, varying according to the nature of the contaminants, the soil chemical-physical properties [3], and the agro-technique (i.e., soil amendment). In this Special Issue, Hailegnaw et al. [18] present their results about biochar, which was proved to reduce Zn, Cu, Mn, and Cd mobility in soil thanks to the modification of pH, CEC (Cation Exchange Capacity), DOC (Dissolved Organic Carbon), and exchangeable Ca²⁺ and K⁺ content in treated soils.

Additionally, plant activities (i.e., root uptake, rhizosphere effects) can modify PTE availability. Agrelli et al. [6] demonstrated that Indian mustard used for phytoextraction significantly reduced bioavailable Zn and Cd concentrations in soil due to plant uptake and soil pH changes, while a lower uptake of Cr and Pb was detected.

Different methods have been proposed for the evaluation of contaminant bioavailability [3], but the most used are extraction in $1 \text{ M NH}_4\text{NO}_3$ (2 h of extraction in a soil–extractant ratio of 1:2.5) and in EDTA at 0.05 M and pH 7 (1 h of extraction in a soil–extractant ratio of 1:10) for measuring readily and potentially bioavailable amounts of PTEs, respectively.

An integration of the information deriving from PTEs bioavailability measured with the extraction methods can be obtained with the bioassays presented in this Special Issue by Duri et al. [5]. By their approach, the health risks for consumers can be evaluated in contaminated hot spots growing food plants which are able to accumulate PTEs, such as lettuce (*Lactuca sativa* L.), perennial wall rocket (*Diplotaxis tenuifolia* (L.) DC.), spinach (*Spinacia oleracea* L.), chicory (*Cichorium intybus* L.), and measuring PTEs content in the edible tissues [6]. Then, the dietary risk can be evaluated by several international methods, such as the HQ methods, where HQ = ADD/RfD; ADD is the average daily dose (mg kg⁻¹ day⁻¹), and RfD is the chronic reference dose of each PTE (mg kg⁻¹ day⁻¹). HQ values > 1 indicate a potential health risk for consumers of food produced in potentially contaminated sites.

Phytoremediation can be done with different approaches. Phytoremediation is the use of plants for reducing concentration (i.e., rhizodegradation and phytoextraction) or risk (i.e., phytostabilization) due to the presence of bioavailable contaminants in the soil [1].

Phytostabilization with poplar (*Populus trichocarpa* × *deltoides* cv. Beaupré) and black bent (*Agrostis gigantea* Roth), aided by soil amendment (i.e., dolomitic limestone and compost), reduced the PTE concentration in leachates and its toxicity towards bacteria, inducing positive changes in the microbial communities of the soil leachates [11].

Inoculation with plant-growth-promoting bacteria (PGPB) is another environmentally friendly and effective tool for improving plant survival and element phytostabilization or extraction under low-fertility conditions. In this Special Issue, Saran et al. [12] present their results with *Bacillus paramycoides* ST9, *Bacillus wiedmannii* ST29, *Bacillus proteolyticus* ST89, *Brevibacterium frigoritolerans* ST30, *Cellulosimicrobium cellulans* ST54, and *Methylobacterium* spp.

Compost and a microbial consortium (arbuscular mycorrhizal fungi, PGPB such as *Bacillus* spp. and *Trichoderma* spp.) was used by Visconti et al. [13] to improve turfgrass growth and soil cover in a heavily contaminated industrial soil. At the same time, Pb and Cd mobility was reduced, highlighting that assisted phytostabilization is a reliable and

effective practice to protect and restore soil biological fertility and to reduce the risk of PTE dispersion in the surrounding environment.

As regards phytoextraction, many studies have demonstrated that some crops are able to accumulate PTE in their biomass, thus reducing the bioavailable content in the soil [9]. Among these species, Indian mustard (*Brassica juncea* (L.) Czern.) has been widely used. This species was found to reduce the bioavailable content of Cd in agricultural soil [6] and has also been suggested for the phytoextraction of Zn [10]. The same authors demonstrated that the mixed cultivation of hyperaccumulator species with legume crops is able to increase the phytoextraction capacity [10].

The use of plants can also be addressed to stimulate the biodegradation of organic contaminants. Pawlik et al. [14] present their results with the pre-inoculation of ryegrass caryopses with a consortium made up of *Rhodococcus erythropolis* 5WK and *Rhizobium* sp. 10 WK for improving the phytodegradation of petroleum hydrocarbon.

Ptaszec et al. [15] propose a multiway enhanced bio- and phytoremediation with ryegrass (*Lolium perenne* L. cv. Pearlgreen) treated with *Rhodococcus erythropolis* CDEL254 strain and a rhamnolipid solution produced by *Pseudomonas aeruginosa* with the aim of increasing the degradation of petroleum hydrocarbons from an aged and highly polluted soil (hydrocarbon content of about 2.5%).

Valorization of biomasses from phytoremediation can improve environmental and socialeconomic benefits. Various environmentally safe technologies have been studied to limit the landfill disposal of biomasses produced in phytoremediation plants by converting them into renewable energy or materials, thereby improving the economic and environmental efficiency of the remediation process within a circular economy perspective [1].

Biomass from phytostabilization or phytodegradation plants usually contains low levels of contaminants, allowing for an environmentally safe energy conversion with thermal treatments. In contrast, crops used for the phytoextraction of bioavailable contaminants (e.g., PTEs) can accumulate an excessive amount of PTEs in their biomass [1]. In this case, direct combustion can be hazardous due to the volatilization of contaminants exposed to high temperature, and pyrolysis for producing char, pyrolytic oil, and syngas is considered more viable. In particular, slow pyrolysis was found to be the more environmentally safe technology since it concentrates and immobilizes PTEs in the solid fraction (char) [19].

In this Special Issue, Carrino et al. [16] point out that biodiesel production from oleaginous crops can drive the agronomic valorization of degraded environments. The authors consider castor bean as one of the most promising crops, since it accumulates PTEs in shoots rather than in oil seeds and can grow on marginal lands not suitable for food crops, thus avoiding competition for land and indirect land use change (ILUC).

Nevertheless, national legislations must be adapted to the concept of end-of-waste [20] in order to remove barriers that limit the recycling of biomasses produced in phytoremediation plants which instead could improve the environmental and social-economic benefits of contaminated sites remediation.

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