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Comparative Evaluation of Technologies at a Heavy Metal Contaminated Site: The Role of Feasibility Studies

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Abstract: Many agricultural areas are contaminated by heavy metals to such a level that the growth of plants is drastically reduced. Based on the site's specific characteristics, feasibility studies were carried out to choose the most effective technologies. Feasibility tests showed that soil washing and phytoremediation technologies could be used at the agricultural site under study. The efficiency of the technologies is highly dependent on soil characteristics, which determine the chemical form of the metals. The results indicate that water-based soil washing can be successfully used with the possibility of reaching the remediation objectives quickly. However, the technology in the first step essentially breaks down the soil. Moreover, phytoremediation cannot be used directly to overcome the toxicity derived from the very high bioavailability of the heavy metals. Still, there is the need to use "assisted" phytoremediation by adding compost that reduces metal bioavailability, allowing phytoextraction. In this case, a longer time is needed to reach the remediation target. The results provide a preliminary scenario for decision-makers and stakeholders to assess possible technologies applicable and a possible scheme to be applied in similar cases of polluted agricultural areas.

Keywords: heavy metals; phytoremediation; soil remediation; sustainable remediation; soil washing; bioavailability

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1. Introduction

Protecting the soil environment, which is related to economic development, is one of the most critical concerns in all countries. Nowadays, most activities that are part of modern human society can result in a direct or indirect release of organic and inorganic pollutants into the environment from the process industry, transportation, and agricultural practices, to name a few [1,2]. These practices, too often accompanied by an incorrect waste disposal policy without adequate recovery of resources [3,4], result in increasingly significant effects on the ecosystem and human health [5].

In an effort to limit these problems as much as possible, a wide range of physico-chemical and biological approaches have been developed for the recovery of contaminated water [6–9] and soils [10–13]. In this regard, remediation of contaminated sites is an important activity that requires effective technological approaches and cost-efficient solutions to restore and preserve soils that would otherwise be lost definitively [14,15].

The primary source of heavy metals in the environment mainly originates from mining activities. Extractive metallurgy is carried out with extremely aggressive reagents, which leads to the production of by-products and residues that greatly influence the quality of soils [16] and surface waters [17–19]. Heavy metals are among the most common pollutants in contaminated sites [12,13,20,21] due to their non-biodegradability and high persistence in the soil. Therefore, there is an urgent need to eliminate or at least reduce the hazards derived from the presence of heavy metals in the soil to avoid uncontrolled pollutant migration [22], given that soil is the environmental matrix that plays an essential role in protecting groundwater and the food chain [23,24]. Soil metal concentrations acceptable for human health and environmental protection need the development of health risk-based soil quality criteria on a site-specific basis [25,26].

Multiple metal contamination is often found in contaminated industrial sites where it is possible to operate with drastic treatments. The problem is even more challenging if the metal contamination concerns agricultural areas where high soil quality is required after reclamation [27]. If the primary sources of heavy metal contamination in agricultural soils are industrial activities and not common agricultural practices, such as the use of fertilizers and pesticides, the remediation is complex and requires additional preliminary tests. The present study focuses on a site contaminated with nickel (Ni), zinc (Zn), and cadmium (Cd) in an area with high agricultural production. The soil concentration of other metals such as lead (Pb) and chromium (Cr), which potentially derived from industrial wastes, were below the limit of Italian legislation for contaminated soils [28].

The site presents complex contamination since the primary source of heavy metals in this soil was the release of waste from the neighboring smelter and other metallurgic industries, severely degrading the soil quality and agricultural yield. In these cases, a feasibility study is essential to assess the viable alternatives that meet the remediation objectives [29–31].

Concerning the specific metals involved, Zn is an essential element for plant growth, as it carries out vital functions in many metabolic pathways. However, excess Zn in soils can reduce plant growth, influencing photosynthetic and respiratory activities and other physiological processes [32,33].

Although Ni is essential in plant metabolism, its increasing concentration in soils can be toxic to many plant species if present in excessively bioavailable forms. It may impact human health through the food chain [34,35].

Cadmium is considered one of the most toxic metals and can seriously threaten human health [36]. Cadmium is on the list of priority pollutants, and it can be hazardous to food safety, even if present in low but bioavailable concentrations in the soil plant system [37].

This work on feasibility studies aims to provide adequate knowledge for screening the most effective remediation technologies and procedures. The screening of technologies to select cleanup alternatives is based on soil characteristics, heavy metal concentration, and chemical forms. Each potential technology is evaluated to make sure it is technically feasible for the contaminated soil under study.

The work was organized starting with a search for knowledge about the origin of the contamination. The characteristics of the soil and their effect on the chemical form of the heavy metals have been determined. Through these site-specific values, it was possible to consider the choice of technologies among those available for these contaminants.

The feasibility tests have limitations deriving from the small scale of the experiments, but the advantage of providing essential answers for the feasibility of remediation in a very short time.

2. Materials and Methods

2.1. The Site

The study site covers 5 hectares within an agricultural area in northern Italy where residues from metallurgic industries have been released in soils and ditches whose waters have been used for irrigation for more than 20 years, until 2010. These improper disposal practices led to soil contamination by Zn, Ni, and Cd.

2.2. Soil Analysis

In the contaminated area, 15 sampling points were identified. Each sample (20 kg) was collected to form a composite sample, which was homogenized and divided for analysis and feasibility tests according to Italian legislation [28]. Further samples were collected from neighboring soil with identical characteristics that had not been affected by the contamination (N-soil).

For the soil analysis, samples were air-dried at room temperature and sieved through a 2 mm sieve for soil characterization and metal analysis. Soil pH was determined using a glass electrode at a soil/water ratio of 1:2.5 [38], cation exchange capacity (CEC) using barium chloride (pH = 8.1) [39], and texture (sand, silt, and clay) by the pipette method [40]. Wet combustion determined organic matter [41].

The evaluation of metal extractability is essential for selecting the best technologies for the specific site, and a sequential extraction procedure (SEP) was thus used. The SEP involved using H_2O, KNO_3, and EDTA sequentially, with a soil: extractant ratio of 1:5 and stirring time of 3 h for each extraction step [42–45]. The extracts from each step were analyzed after centrifugation and filtration.

2.3. Soil Washing Feasibility Test

Samples of 1 kg of soil were subdivided into sub-samples of 250 g and submitted to a bench-scale soil washing test according to the previously described procedure [42,45].

(1) To make a slurry, water was added to the contaminated soil sample in a liquid-to-solid ratio of 3:1 (defined after preliminary experiments) in 2 L plastic vessels.
(2) To detach the finer particles from the coarser ones, the slurry was shaken at 20 °C overnight in a high-speed agitator to enable the vigorous brushing of the soil particles.
(3) The slurry was then screened using different sieves to separate the soil particles by size.
(4) At the end of the test, the contaminated soil was separated into the following fractions: >5 mm, 5–2 mm, 2–0.2 mm, 0.2–0.1 mm, 0.1–0.063 mm, <0.063 mm.
(5) Each fraction was recovered and weighed after oven drying at 105 °C, and Zn, Cd, and Ni were determined in each fraction from the test and in the washing water using inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Liberty AX Varian spectrometer.

2.4. Phytoextraction Feasibility Test

Considering that in the polluted soil, the low pH value and high level of metal concentration drastically hindered healthy plant growth, 10% compost was added to the soil to reduce the negative effects of phytotoxicity. This amount was selected based on the phytotoxicity test with *Lepidium sativum* L. [46]. The phytotoxicity test was performed when increased compost was added to the original soil. The germination index ($GI\%$) was calculated according to Equation (1), where G_s and G_c are the average number of germinated seeds in the contaminated soil samples and the negative control, respectively. At the same time, L_s and L_c are the mean root lengths (mm) for the contaminated soil samples and the negative control, respectively.

$$GI\% = \frac{G_s \times L_s}{G_c \times L_c} \times 100 \quad (1)$$

Green compost is derived from a source-separated collection (vegetal waste). Due to the very low content of heavy metals, it is considered a fertilizer and, therefore, can be freely sold and used in agriculture. The total organic carbon content of the compost, as provided by the seller, was 350 g kg^{-1} dry weight (d.w.), total nitrogen 15.6 g kg^{-1} d.w, pH 7.9, and total Cd, Ni, and Zn concentrations of 0.22, 1.5, and 3.9 mg kg^{-1} d.w., respectively.

After one week of compost equilibration in the soil, the treated soil was analyzed for pH, total and bioavailable metal concentration to determine any possible modifications.

The experimental conditions of the phytoremediation feasibility test were the following:

- Mesocosms with 3 kg of original, untreated soil (U-soil);
- Mesocosms with 3 kg of 10% compost-treated soil (T-soil);

- The mesocosms were sown with 1.5 g of *Brassica juncea* seeds or 10 seeds of *Zea mays* per pot;
- Daily irrigation according to the needs of the plants;
- Pots are equipped with a leachate collector to evaluate the possible leaching of the metals.

All experiments were carried out in triplicate for a total of 12 mesocosms in a greenhouse, maintained at 18–25 °C with natural day/night cycles for the duration of the experiment. The experiment lasted 60 days, after which the plants were harvested, and their biomass production was evaluated. Aerial parts and roots were separated and washed with deionized water. The roots were washed in an ultrasound bath (Branson Sonifier 250 ultrasonic processor; Branson, Danbury, CT, USA) for 10 min to eliminate soil particles that could have remained on radical surfaces. Samples were then dried in a ventilated oven at 40 °C until constant weight, and the dry weight of tissues was determined gravimetrically. Shoots and roots were analyzed for Zn, Ni, and Cd content.

2.5. Metal Analysis

The determination of heavy metals in soil and plant samples was performed according to the US-EPA method 3051-A [47] and US-EPA method 3052 [48], respectively. The metal concentration in soil, plants, soil fractions, washing water, and extracts from SEP was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Liberty AX Varian spectrometer. All data reported are the average of three replicates.

2.6. Quality Assurance and Quality Control

Quality assurance and quality control were performed by testing two standard solutions (0.5 and 2 mg L^{-1}) for every 10 samples. CRM ERM–CC141 for soil and CRM ERM–CD281 for plants were certified reference materials. The values obtained for Cd, Zn, and Ni were in agreement with the certified values. The detection limits for Cd, Zn, and Ni were 0.3, 1.7, and 8 µg L^{-1}, respectively.

2.7. Statistical Analysis

Statistical analysis was performed by Statistica v. 6.0 (StatSoft, Inc., Tulsa, OK, USA). The data were analyzed using a one-way analysis of variance (ANOVA). The Tukey Honestly Significant Difference test [49] was used for pairwise comparison of means at 0.05 significance levels ($p < 0.05$).

3. Results and Discussion

The untreated contaminated soil (U-soil) was characterized by a pH value of 5.22, a CEC of 21.4 cmol kg^{-1}, and the following texture: sand 48.4%, silt 46.0%, clay 5.6%, and organic matter of 3.7%. The mean concentrations of Cd, Zn, and Ni were 22, 310, and 163 mg kg^{-1}, respectively.

In soil treated with green compost (T-soil), the texture characteristics, CEC, and total metal concentrations did not change, but the soil pH increased from 5.22 to 6.11. T-Soil was used only for the phytoremediation test.

Several fully developed technologies are available for the remediation of heavy metals in soils. In the case under study, the best applicable technologies were evaluated according to the feasibility flow chart reported in Figure 1.

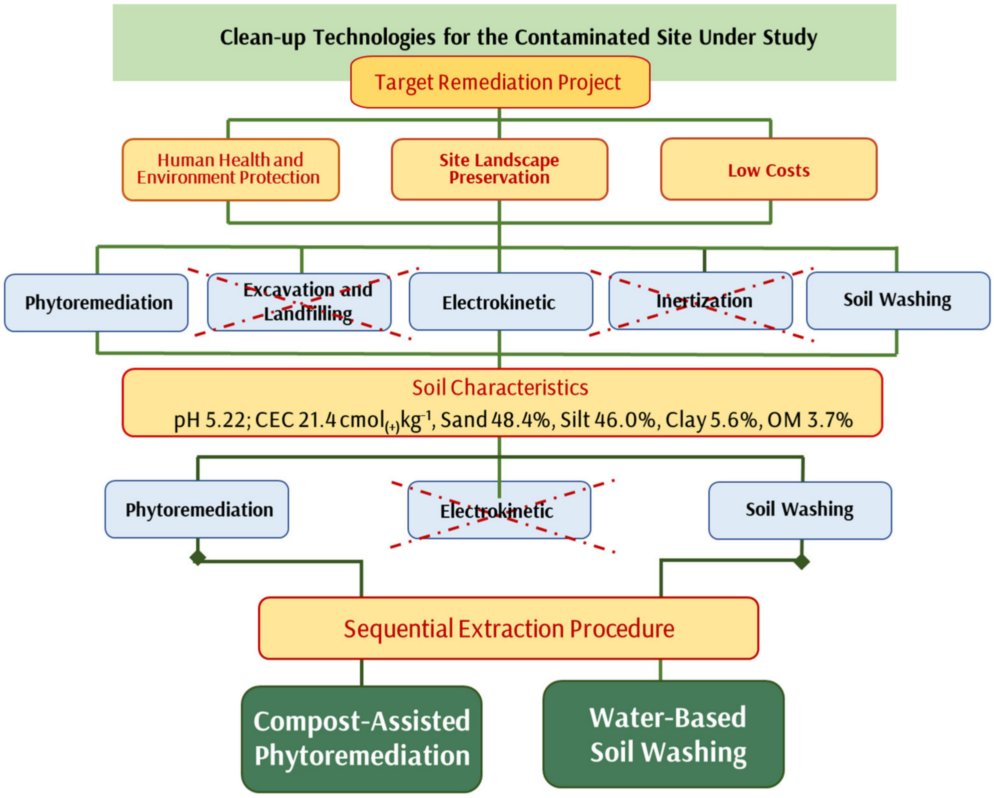

Figure 1. Scheme of technologies screening based on soil properties of the contaminated soil.

The remediation project identified three priorities: human health and environment protection, preservation of landscape site, and remediation interventions at sustainable costs.

The consolidated alternatives, such as inertization [50] or excavation and landfilling, were excluded due to the excessive cost involved. Thus, two technologies were discarded. The remaining technologies were then examined based on the specific characteristics of the contaminated soil. The low clay content indicated the relevant difficulty of using electrokinetic remediation (EKRT) [51–53]. The best remaining technologies were thus soil washing and phytoremediation. Based on the results of the SEP, the chemical forms of the metals were identified in order to define the possible site-specific solutions to be submitted to the final decision-makers.

Soil washing is an ex situ remediation treatment based on soil particle size separation by scrubbing, which separates the finer particles (<2 mm), which are generally more polluted, from the coarser particles (>2 mm) of the soil, which are generally less or non-contaminated. The contaminants are preferentially adsorbed on finer grain-size materials, such as clay or humic substances, with a greater specific surface area. At the end of the process, the cleaned materials are recovered and can be reused on the site. Most heavy metals are concentrated in a small volume of the finest fractions, which can be disposed of in landfill or subjected to further treatments after dewatering. It must be underlined that the term "soil washing" refers primarily to the water-based physical separation process. However, it is also often described as a chemical extraction method, which is much more expensive due to the cost of reagents [54–56]. Recent economic estimations indicate that chemical reagents increase the cost of technology by about ten times [57–59].

Phytoremediation includes phytoextraction, phytostabilization, rhizodegradation, phytodegradation, phytotransformation, and rhizofiltration [60,61]. In heavy metal polluted soils, phytoextraction can be an effective "green remediation" solution [62,63], which removes the metals without destroying the soil structure and fertility. This technology is based on the metal uptake capabilities of plant root systems and their ability to translocate the metals into harvestable shoots. Phytoextraction can involve hyperaccumulator species that naturally accumulate and transfer high amounts of metals to shoots. If it is not possible to use hyperaccumulating species, often specific for each metal, it is possible to resort to "assisted" phytoremediation [64]. Assisted phytoremediation is based on modifying the soil's chemical environment by adding substances that modify metal bioavailability [63,65,66].

Both phytoremediation and soil washing strictly depend on soil properties, which determine the chemical forms of metals in the soil. The next step in the feasibility flow chart was thus to evaluate the solubility and bioavailability of heavy metals by SEP.

The evaluation by SEP of metal extractability is an essential step in the phytoextraction feasibility test since plants can take up only bioavailable metals. SEP is also essential for selecting the washing liquid for the soil washing test. Figure 2 shows the results of the SEP for both the original, untreated soil (U-soil) and the soil treated with green compost (T-soil) aimed at assessing the changes in the bioavailability of metals resulting from the addition of compost.

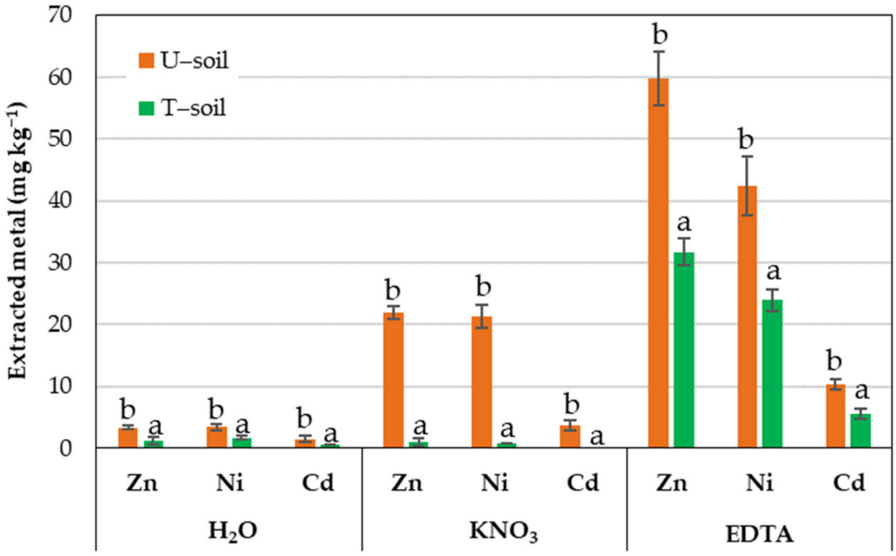

Figure 2. Concentration (mg kg^{-1} dry weight) of metals extracted by the sequential procedures in different soil samples. Data are expressed as the means ± SD (n = 3). Different letters indicate significant differences ($p < 0.05$) in concentrations between U-soil and T-soil in each fraction of the SEP.

The first step of the SEP revealed that the original, untreated soil was characterized by a high concentration of metals in soluble form (from about 1.5 mg kg^{-1} for Cd to about 3.5 mg kg^{-1} for Zn and Ni). The metal water-soluble concentrations in the neighboring unpolluted soil (N-soil) of the investigated metals were always lower than 0.1 mg kg^{-1}; thus, the results obtained reflect the soil's pollution state well. The concentration of soluble metals, which are readily bioavailable, may have caused phytotoxicity that hindered plant growth. Adding compost to the soil reduced the amount of water-extractable metals by 64%, 80%, and 50% for Cd, Zn and Ni, respectively.

The second step of SEP extracted the "exchangeable" metals retained by soil surfaces with low-energy electrostatic linkages. These extractable amounts were very high in the U-soil, ranging from 3.7 mg kg^{-1} for Cd to 21.3 mg kg^{-1} for Ni and 21.9 mg kg^{-1} for Zn. In contrast, the exchangeable concentration in the N-soil was nearly 10 times lower. The addition of compost substantially decreased the exchangeable metals with a more than 90% reduction for all three metals.

The last step, which identifies the metals bound by linkages also of a covalent nature, showed concentration values varying from about 10 mg kg^{-1} for Cd up to about 60 mg kg^{-1} for Zn, while Ni had a value near 40 mg kg^{-1}. These values are also about 10 times higher than those of the N-soil. Compost addition produced a clear decrease in the concentration of EDTA-extractable metals.

3.1. Results from Soil Washing Test

The results of the SEP highlighted that water could be used as a washing solution without resorting to more invasive and expensive extractants.

In fact, the soil washing test separated the soil into different fractions with the following weight distribution: 61% of the total soil weight was recovered in the size fraction >5 mm and the finer fractions: 14% in 5–2 mm, 11% in 2–0.2 mm, 1% in 0.2–0.1 mm, 2% in 0.1–0.063 mm, and 11% in the size fraction < 0.063 mm (Figure 3).

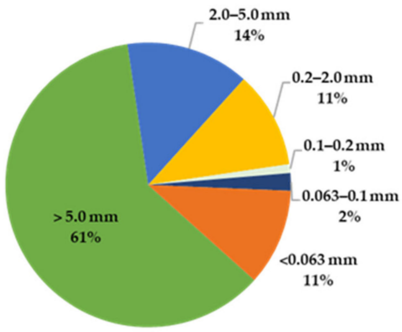

Figure 3. The percentage weight distribution of size fractions from the soil washing test.

After soil washing, the heavy metals were mainly found in the finer soil fractions (Figure 4). In contrast, their concentrations in the coarse fraction of the soil were below the target values [28].

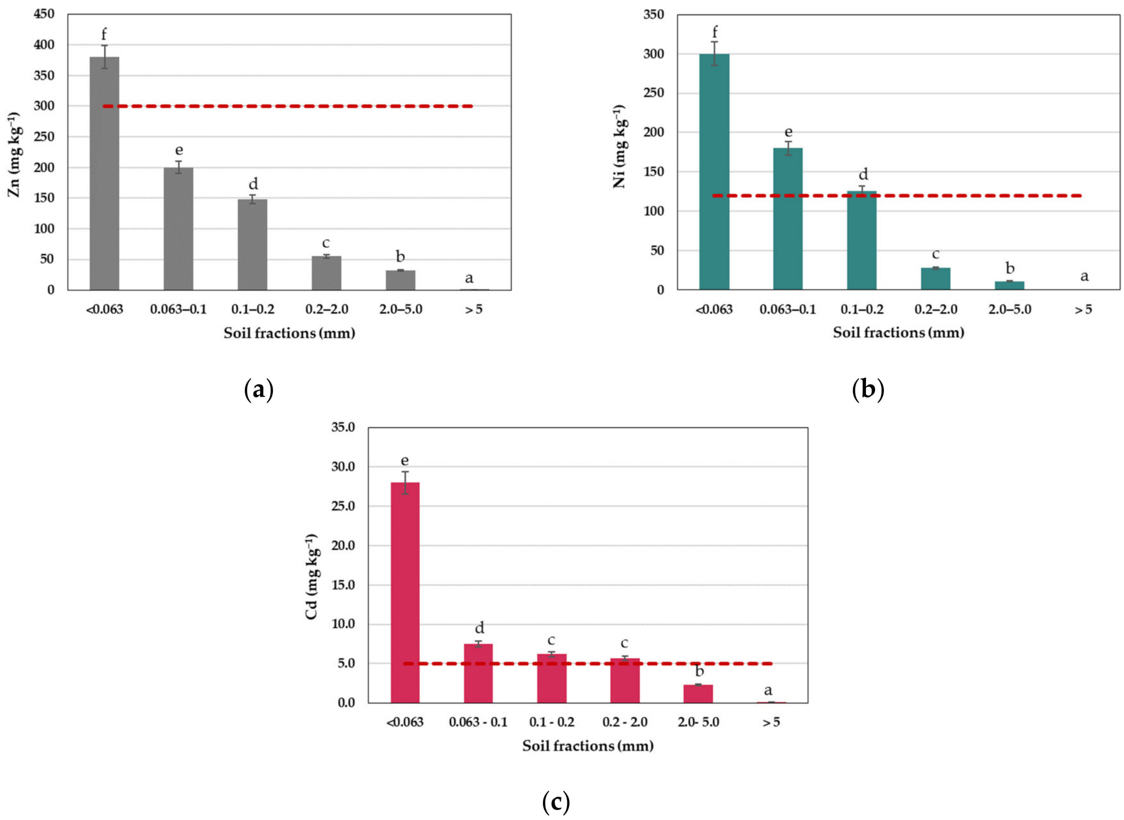

Figure 4. Zn (**a**), Ni (**b**), and Cd (**c**) concentration (mg kg^{-1}) in the different soil size fractions (mm). Values are expressed as the means of the three replicates (±SD). Different letters indicate significant differences ($p < 0.05$) between metal concentrations in the fractions from soil washing. The red dotted line is the remediation target for each metal.

The resulting division of soil into different levels of contamination considerably reduced the volume of the effectively polluted soil. It highlighted the possibility of immediate reuse of a large part of the decontaminated soil. Considering the percentage distribution by weight of the contaminated soil, it was evident that more than 60% of the soil could be immediately reused after the soil washing treatment.

As for Zn, in the fraction 0.063–0.1 mm, the concentration of 200 mg kg^{-1} was below the remediation limit, and the concentration values in the other fractions were characteristic of uncontaminated Italian soils.

In the size of particles 0.063–0.1 mm, the Ni concentration was 180 mg kg^{-1}. In the fraction 0.1–0.2 mm, the values decreased to 126 mg kg^{-1}, which was very near the remediation target (120 mg kg^{-1}). The Cd concentrations were below the remediation target only in the fraction 2.0–5.0 mm; however, in the other fractions, the concentration values were not far from the remediation limit (5 mg kg^{-1}).

From the feasibility test, the soil washing efficiency also appeared very high because, in the washing water, the concentration of metals was still low (below 5 mg L^{-1}), and the purification of these waters does not present particular problems, either technical or economic [67].

Thus, soil washing is an appropriate remediation technology for this contaminated site. The results agree with previous findings of heavy metal contaminated soils [68], and the removal of pollution may be performed relatively quickly with the major part of the treated soils that can be reused at the site.

The kind of washing solution used in the treatment can drastically influence the properties of the original soil, such as the humic material and nitrogen content [69–71]. There is increasing awareness among the scientific community [67,72] and governments [73–75] that strong washing solutions should be avoided as they can irreversibly affect soil components and quality. Thus, the technology has been used as a physical separation process. Moreover, using water as a washing solution can minimize the detrimental effects on the post-remediation soil quality and prevent the problems derived from using strong reagents.

3.2. Results of Phytoextraction Feasibility Test

As previously stated, one of the main problems of the site under study was the high concentration of heavy metals in the soil, coupled with the acidic pH value. Consequently, the high bioavailability of the metals in some areas hindered the ability of the contaminated soil to support vegetation.

The species *B. juncea* and *Z. mays* were chosen for the phytoremediation test due to their ability to tolerate and accumulate high amounts of various heavy metals from contaminated soils in their tissue [76–79]. However, in the original, untreated soil (U-Soil), at the end of the growth period, the biomass production of the two species was very low, with average values of 2.34 mg for *Z. mays* and 1.78 mg for *B. juncea*.

The sequential extraction results showed the high mobility of heavy metals in the original soil since great amounts of metals were extractable by water and KNO_3. These metals, present in soluble and exchangeable forms, are easily bioavailable and contribute to promoting conditions of phytotoxicity. In addition, soils that have been abandoned for years lose their fertility due to the toxicity derived from heavy metals and the decrease in quality derived from the decrease in vegetative cover [80,81]. In this case, the large areas on which the plants did not grow led to the assumption that the high bioavailability of the metals could create phytotoxic phenomena. In similar circumstances, one phytoremediation strategy is to modify the pH of the soil with the addition of suitable materials [43]. Therefore, exploiting the experience acquired in similar situations [43], it was considered appropriate to modify the soil environment by adding a low-cost material such as compost. The 10% amount of compost added was selected based on the phytotoxicity test (Figure 5), which showed that greater amounts of compost did not change GI%.

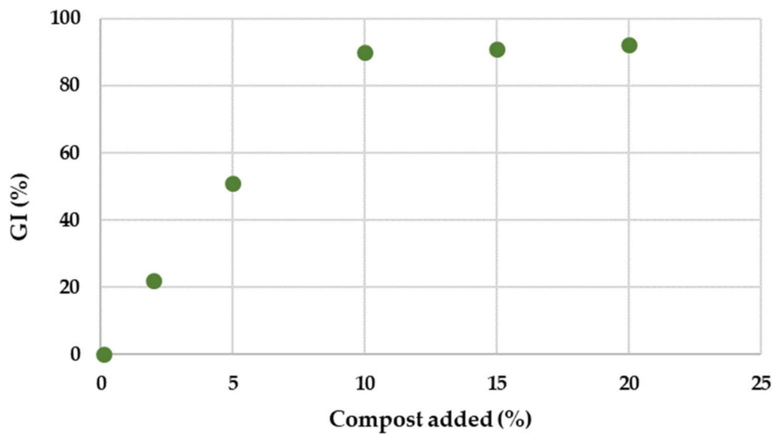

Figure 5. Variation of Germination Index (GI%) at increasing compost addition.

The addition of green compost created more favorable conditions for the growth of plants, decreasing metal bioavailability, as shown by the SEP results, due to the increase in soil pH from 5.22 to 6.11, which reduced the metal concentrations in the soil solution. The reduced solubility of metals greatly increased the biomass production of both plant species; the mean values increased from 1.78 to 129 mg for *B. juncea* and from 2.34 to 915 mg for *Z. mays* grown on T-soil. Using green compost also probably improved the soil conditions and added fertility elements such as carbon, nitrogen, and phosphorous to the contaminated soil.

Compost-assisted phytoremediation was also very efficient in decreasing the heavy metal uptake by the plants. The concentrations of Cd, Zn, and Ni in the aerial parts of plants were nearly 80% lower than in plants grown in the original, untreated soil. Although the decrease in metal concentration in plants may seem in contrast to the phytoextraction, this decrease resulted in a high increase in biomass production in the soil, which originally had been unable to support plant growth. In a soil where the high concentration of metals in bioavailable form prevents normal plant growth, the best combination between biomass production and plant uptake of metals should thus be first considered in a feasibility test aimed at identifying the appropriate technology for the specific contaminated site.

The efficiency of the technology can be obtained by considering the results of two dynamic processes: the shoot biomass production and the heavy metal uptake by plants. Therefore, the total uptake (Figure 6) needs to be evaluated, expressed as the product of the concentration of metals in the plant and the biomass produced [82,83].

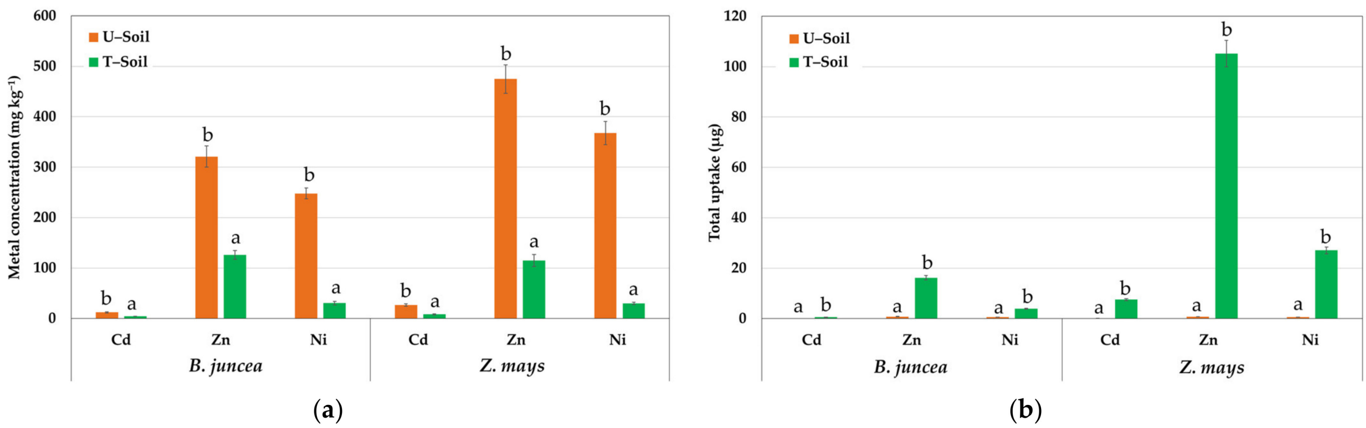

Figure 6. The contrasting trend of metal concentration (mg kg^{-1}) in the shoots of plants (**a**) and total uptake (μg) (**b**) in original, untreated soil (U-soil) and compost-treated soil (T-soil). Different letters indicate significant differences ($p < 0.05$) between U-soil and T-soil.

The total uptake values show that treatment with green compost led to much greater removal of metals. The amount of Cd accumulated in the original soil was approximately 12 times higher for both plants. In comparison, the amount of Ni was approximately 3 times higher for *B. juncea* and 5 times higher for *Z. mays*. After treatment with the green compost, the total accumulation of Zn was approximately 8 times higher for *B. juncea* and 15 times higher for *Z. mays*.

The results of the total uptake indicate that phytoremediation technology can be used after the addition of compost, which makes it possible to obtain healthy plant growth with the production of adequate biomass.

The translocation factor (TF), defined as the ratio between the heavy metal concentration in shoots and the concentration in roots [84], also indicated that compost limits the translocation of metals from roots to shoots (Table 1).

Table 1. Translocation factor of Cd, Zn, and Ni for *B. juncea* and *Z. mays* in original, untreated soil (U-soil) and compost-treated soil (T-soil).

	B. juncea		***Z. mays***	
	U-Soil	**T-Soil**	**U-Soil**	**T-Soil**
Cd	0.54	0.28	0.52	0.47
Zn	0.41	0.17	0.52	0.50
Ni	0.38	0.08	0.40	0.37

The data obtained showed that the concentrations of all three metals (Figure 6) were always higher in the roots than in the shoots. This result highlighted the root system's capacity to stimulate a defense mechanism [85], thereby regulating the metals' translocation to the aerial parts in the original, untreated and compost-treated soil. The data of a feasibility test need to be carefully screened before applying the technology at the field scale to evaluate the effects of the change in scale.

3.3. Selection of Technologies

The low clay content in the soil eliminated potential alternatives such as EKRT, which is less likely to produce the desired results on this site. The remaining technologies, soil washing and phytoremediation, therefore appeared to satisfy the threshold criteria to protect human health and the environment. They were also found to be viable and efficient in the long term.

In the case of acid soils where very high bioavailability of the heavy metals can hinder plant growth, compost-assisted phytoremediation can re-establish vegetation by reducing bioavailability so that phytoextraction can be applied. However, it is difficult to forecast the time needed to reach the remediation target due to the scale-up from the mesocosm to the field.

Moreover, soil washing could potentially rapidly meet the remediation objectives. Although it is very invasive as it decomposes the soil, once relocated on-site, the fertility of the cleaned soil can be restored quickly by adding organic material, such as compost. These considerations also leave another pathway open, which could be the use of both technologies in sequence: soil washing and assisted phytoremediation. In this case, the growth of the plants would certainly reduce the time for the recovery of good soil quality. A similar strategy was positively tested for soil contaminated by heavy metals [86].

A similar comparison through the feasibility tests between soil washing and phytoextraction was previously evaluated for the remediation of a former industrial contaminated soil with completely different characteristics of Pb and As contamination and basic pH [45]. In that industrial soil, the bioavailability of the metals was very low, and it was necessary to add mobilizing agents to promote the phytoextraction process. On the contrary, in this agricultural soil, the too-high bioavailability requires adding a material (compost) capable of reducing the concentration of metals in the soil's liquid phase.

The final destination of the site then becomes the key for selecting technologies. In an area intended for commercial or industrial activities, the choice of soil washing shows positive aspects due to the short time required for reclamation. On the contrary, in an agricultural area, in which the quality of the soil plays a role of primary importance, the choice of green technology, such as phytoremediation, seems more suitable even if the recovery times of the soil can be longer.

However, the technologies will also need to be evaluated based on waste management cost [87,88] capital and annual operating and maintenance expenses, which, in the end, could be the determining factor for the final choice of technology, together with their environmental impact [89].

The technologies screening scheme described (Figure 1) in this paper could also be useful for similar polluted agricultural areas, which, in Europe, are often located in the proximity of large cities [90].

4. Conclusions

The use of soil washing and phytoremediation was evaluated in an agricultural area contaminated by heavy metals to such an extent that plants could no longer grow normally. Feasibility tests were conducted to show how the two technologies could solve the contamination problem at the investigated site. The feasibility studies of technologies offer a remediation scenario that must be evaluated by the stakeholders and national or regional bodies involved in the final decision.

The remediation of contaminated sites is experiencing an important historical moment, and the approach to remediation is changing. We moved from the remediation target based on generic table values to the definition of the target based on risk analysis. However, even this phase is evolving towards choices that favor a lower impact on both the conservation of the environment and the reduction of energy consumption through an increasingly site-specific perspective.

Feasibility tests are called upon to play a fundamental role to offer the final decision-makers a range of technological choices that must be carefully evaluated on the basis of the specific conditions of the site in question. From this point of view, the scheme proposed in this work can be useful for modulating the most appropriate choices in relation to the specific characteristics of the soils involved. Without specific attention to the characteristics of the soil, a generic assessment of technologies risks being completely unsuccessful.

Future research will also have to face the challenge of a choice based on the adaptability of technologies to the potential effects of climate change.

The contaminated soil characteristics are the basis for selecting the remediation technologies, and all attempts should be made to use low-cost, environmentally friendly materials for assisted phytoremediation and washing solutions. In the case of soil washing, the cost can be reduced using the technology as a water-based physical remediation, which can drastically reduce the costs of the process and make it easier to restore the functionality of the soil relocated to the site. In the case of phytoremediation, adding compost improved the soil quality and, as a low-cost, waste-derived material, can also play an important role from the perspective of the circular economy.

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