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Assessing Environmental Sustainability of Phytoremediation to Remove Copper from Contaminated Soils

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Abstract: Phytoremediation stands out as a promising technology for removing heavy metals from contaminated soils. This work focuses on studying the environmental performance of phytoremediation in removing copper from contaminated soil located in an old Spanish mine using the life cycle assessment (LCA) method. For this purpose, *Brassica juncea* (brown mustard), *Medicago sativa* (alfalfa) and their rotary cultivation were assessed along with different options for managing biomass (landfill disposal and biomass cogeneration). In addition, soil excavation and soil washing treatments were also compared to phytoremediation. *M. sativa* proved superior to *B. juncea* and their rotary cultivation, regardless of the biomass disposal option, achieving impact reductions of 30–100%. This is due to the ability of *M. sativa* to fix nitrogen, which reduces fertiliser requirements. Among the biomass management alternatives, cogeneration was superior to landfill disposal in all cases by allowing for energy recovery, thereby reducing environmental impacts by 60–100%. *M. sativa* + cogeneration is the option that presents the best environmental performance of all the studied treatments, achieving reductions up to negligible values in four of eight impact categories due to the impacts avoided by energy production. On the contrary, soil excavation is the less desirable option, followed by soil washing treatment.

Keywords: phytoremediation; phytoextraction; life cycle assessment; soil remediation; copper removal

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1. Introduction

The current concern on sustainability allows for governments to take actions in order to mitigate the effects of different impacts, including greenhouse gas emissions, soil contamination, air and water pollution, depletion of natural resources, etc., on the environment and human health [1,2]. In this sense, sustainability is being progressively included in the policy priorities of many countries through the Sustainable Development Goals (SDGs) of the 2030 Agenda adopted by all United Nations Member States [3]. Concerning SDGs 3, 7 and 15, the remediation of metal-contaminated soils contributes to improve the quality of life of the population and the environment within the framework of global sustainability.

Heavy metals, like cobalt, copper or chromium, are trace elements essential for plants as micronutrients. However, an excess of these elements causes harmful effects on the growth of plant species and on human health through food chains, as plants can accumulate metals from contaminated soils [4,5]. It is well known that mining activities cause considerable adverse environmental and human effects due to harmful metal contamination [6,7]. This industry generates a large amount of waste rocks, ore dust, etc., which often contain various trace metals that cause soil contamination [8,9]. In this context, soil contamination by heavy metals is a current worldwide concern because these metals are non-biodegradable. Consequently, governments have established remediation of contaminated soil as a national priority [10–13].

In this regard, most metal-contaminated areas have been treated by two approaches: soil excavated and landfilled as hazardous waste or a soil washing procedure. However, soil is a vulnerable and almost non-renewable natural resource, so in situ and eco-friendly procedures must be addressed [11,14]. In this sense, phytoremediation is an interesting alternative due to its low price and its soil-friendly nature [15]. It is a procedure that harnesses the natural abilities of plants to absorb and eliminate pollutants such as metals, which they can tolerate and accumulate in their leaves and roots [16]. Therefore, phytoremediation emerges as an environmentally friendly method for addressing soil contamination. Particularly, the phytoextraction involves hyper-accumulator plants that can translocate heavy metals to shoots. Thus, metals are eliminated with the harvesting of these plants from the contaminated area [15].

Brasicca juncea (brown mustard) and *Medicago sativa* (alfalfa) are plants widely studied in soil phytoremediation for metal removal. *B. juncea* is a herbaceous plant belonging to the family Brassicaceae. Many studies have demonstrated that *Brassica* species (including *B. juncea*) show a rapid growth rate, high above-ground biomass production and high heavy-metal sequestration ability from contaminated media [15,17–22]. For copper, the bioaccumulation factor (BAF) of the whole mustard plant is 1.81, being 1.01 for the leaves [23,24]. In the same way, *M. sativa* is a perennial herb from the family Fabaceae or Leguminosae. It is a widely cultivated forage crop with an extensive tap-root system. It can easily uptake copper, lead and cadmium from contaminated soils, making it a plant that has recently received attention for phytoremediation studies. The BAF for copper is 3.27 for the whole alfalfa plant and 0.86 for the leaves. Additionally, the alfalfa plants can be harvested several times to obtain a higher biomass yield and show a short growth cycle [25,26].

The rotatory crop consists of a production system in which two or more species are grown successively during part or all of the life cycle. The relevant aspect of this mechanism lies in the different use of resources by the crops that make it up [27]. Following the general principles of crop rotations reported from the literature (the species with high nitrogen demand must be preceded by the cultivation of legumes; the succession of crops must be carried out with species that are not similar or analogous; in the rotation system, species with deep roots should alternate with species with more superficial roots; etc.) [28], it is concluded that the rotation design between *B. juncea* and *M. sativa* constitutes an alternative of great interest. This rotation offers a balance between the main crop, consisting of alfalfa, and the cover crop or green fertiliser, made up of brown mustard. The practice of crop rotation has been widely studied as an environmentally friendly activity that contributes to the sustainable use of agricultural land because it has the potential to address ecological problems, such as degradation of soil structure and loss of soil organic carbon [29–31]. However, it does not have to be the best procedure for soil contaminated with metals.

In the present work, the study of the continuous monoculture of *B. juncea* and *M. sativa* as well as the study of rotational cultivation of both herbs as soil phytoremediation plants are studied from an environmental view with the life cycle assessment methodology (LCA) since the environmental sustainability of soil remediation processes is a key aspect. LCA is a systematic, standardised tool to determine the environmental feasibility of soil remediation technologies as it is widely demonstrated in the literature [32–36].

The environmental impacts of *B. juncea* and *M. sativa* monocultures and rotatory-culture scenarios for soil remediation were quantified, combined with different final uses of biomass: security landfill disposal and energy recovery (this option was simulated). On the other hand, the LCA of soil washing and excavation was carried out. The former was simulated using SuperPro Designer 9.5, whereas data on the excavation process were adapted from the available resources. The LCA results of the phytoremediation-based scenarios and traditional treatments were compared. The novelty of our work is to provide LCA results on soil remediation, which are usually scarce in the literature, using an engineering approach that can be of interest to be applied to other soil remediation schemes.

2. Materials and Methods

2.1. Soil Description

The soil selected for this study is located in an old mine in Southern Spain (38°06′00″ N 3°40′03″ O), mainly dedicated to mineral extraction. As a result of this activity over time, this soil presents significant contamination by heavy metals, as reported in [37]. Among the different metals, our study is focused on copper as it can be removed by a variety of treatments and its presence in the soil can affect microbial activity as well as agriculture [38]. Therefore, the environmental assessment of treatment for its remediation is of interest. The main characteristics of the soil are taken from [37] who carried out a deep experimental analysis of the soil by collecting a total of 44 samples in an area of 2.2 km^2. Table 1 summarises the values for the soil features considered in our study, calculated as the average of the total samples.

The average Cu content shown in Table 1 exceeds the maximum level of copper in soils established by the local government regulation (595 ppm) [39]. Consequently, the amount of copper that should be removed is 77.23 ppm. Considering the particle size distribution shown in Table 1, the soil falls within clayey sand soil [40]. Finally, the average annual temperature of the soil location is 17.1 °C, the humidity is 59.3%, and the annual average precipitation value is (4410.3 m^3/hm^2) [41].

Table 1. Main characteristics of the studied soil.

Parameter	Value
pH	6.8
Density [a] (kg/m^3)	1600
OM [b] (%)	2.35
Cu content (ppm)	627.23
Sand (%)	72.5
Silt (%)	5.9
Clay (%)	21.6
Soil type [c]	Clayey sand (CS)

[a] Calculated from particle size distribution; [b] Organic matter; [c] According to Unified Soil Classification [40].

2.2. Goal and Scope of the LCA Study

The goal of this work is to analyse the use of phytoextraction with *B. juncea* and *M. sativa* to remove copper from the soil described above. For that purpose, three case studies were analysed: phytoremediation, soil washing and soil excavation. In the phytoremediation scenario, *B. juncea*, *M. sativa* and rotary cultivation of both species were assessed, and two end-of-life biomass scenarios were evaluated for each: security landfill disposal and energy recovery by cogeneration. In addition, copper removal using washing soil and excavation scenarios were also analysed. Table 2 shows the scenarios and case studies assessed in the present work.

Figure 1 shows a general diagram of the different case studies and the steps involved. The system boundaries encompass all inputs and outputs of the processes, whereas capital goods are excluded from the study.

The labour machinery used for cultivation operations (ploughing, harrowing, sowing and harvesting) is considered in the phytoremediation case and was calculated using the spreadsheets reported by the Spanish Government for agricultural labour [42], considering the specific characteristics of the machinery.

Table 2. Case studies considered in this work.

Case Study		Treatment		Scenario
1	Phytoremediation	*B. juncea* (BJ)	Landfill disposal Cogeneration	BJ-L BJ-C
		M. sativa (MS)	Landfill disposal Cogeneration	MS-L MS-C
		Rotatory crop (BJ + MS)	Landfill disposal Cogeneration	RC-L RC-C
2	Soil Washing			
3	Soil Excavation			

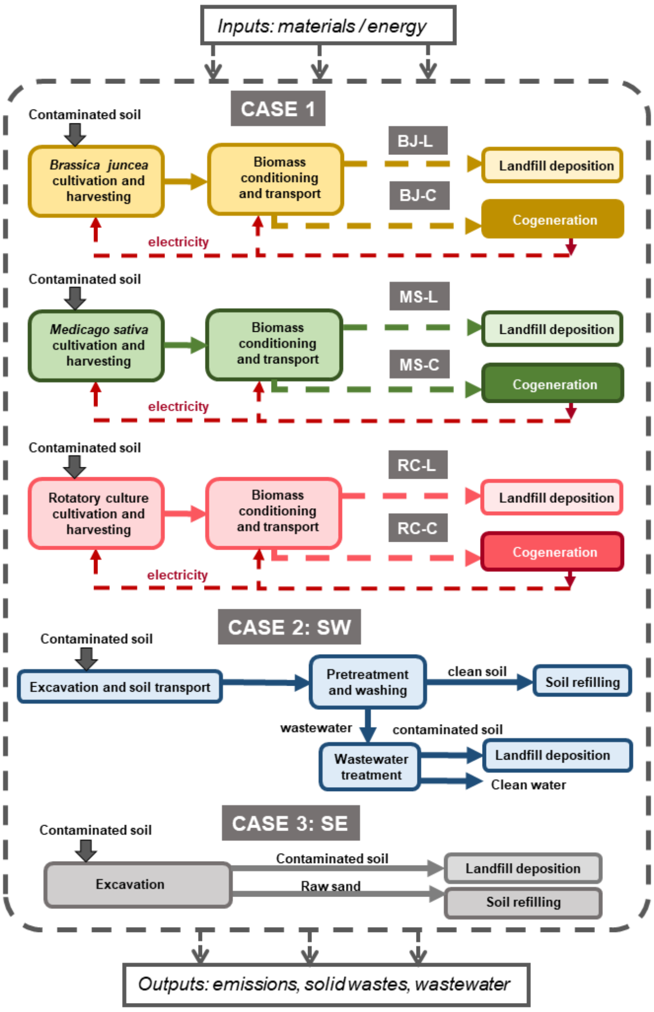


Figure 1. Battery limits for the considered case studies. Case 1: phytoremediation (BJ: *B. juncea*; MS: *M. sativa*; RC: rotary crop; L: landfill; C: cogeneration); Case 2: soil washing; and Case 3: soil excavation.

The functional unit selected for this study is the decontamination of 1 hm^2 of the considered soil (20 cm depth) up to the maximum Cu concentration allowed by government regulations. The amount of soil equivalent to the functional unit was calculated from its density (1600 kg/m^3 for this type of soil [43], see Table 1), resulting in a value of 3200 ton.

2.3. Life Cycle Inventory Analysis (LCIA)

The life cycle inventory data of all treatments were adapted from the literature or calculated by simulation using SuperPro Designer 9.5 (Intelligen Inc., Scotch Plains, NJ, USA). Material and energy production as well as transportation vehicles were adapted from the Ecoinvent database 8.3 and Gabi Professional 2023 database (Sphera Solutions GmbH., Leinfelden-Echterdingen, Germany).

2.3.1. Case 1: Phytoremediation

The main steps involved in the phytoextraction of Cu-contaminated soils using *B. juncea*, *M. sativa* and their combination (rotary culture) are cultivation and harvesting, conditioning and transport and use of the grown biomass, as depicted in Figure 1. In all cases, energy recovery by cogeneration in a CPH system and security landfill disposal were evaluated for biomass end life. According to the flowsheet scheme reported elsewhere, the cogeneration process was simulated using SuperPro Designer 9.5 [32]. On the other hand, landfill disposal was modelled as a security deposit adapted from the LCA databases mentioned above. Table S1 (Supplementary Materials) summarises the detailed inventory of phytoremediation scenarios. The steps involved in both cases are explained below.

i. Cultivation and harvesting: The cultivation of *B. juncea* (BJ), *M. sativa* (MS) and the rotatory culture (RC) was evaluated in the different scenarios of Case 1, and the inventory data are summarised in Table S1.

-BJ: Two annual crops (including leaf cutting per culture) followed by the harvesting of the whole plant are estimated, leading to a total biomass production of 11.2 tons/hm^2·year. Considering the average value of annual rainfall in the studied area, the need for irrigation of B. juncea can be considered negligible.

-MS: This is a perennial crop belonging to the legume family and commonly used as a forage plant; its crop is considered to be annual. During the year, eight leaf cuts are considered (the first cut after 60–65 days and the others after 35–45 days each one), providing a biomass production of 19.4 tons/hm^2·year. This plant needs a total irrigation of 6000 m^3/hm^2 [44], but only 4410.3 m^3/hm^2 can be covered with the average value of annual rainfall, and consequently, an irrigation water volume of 1589.7 m^3/hm^2 should be considered.

-RC: As previously described, the rotatory crop design between BJ and MS forms an alternative of great interest. Thus, a temporal distribution of two periods of three months (from March to May and from September to November) was considered for the mustard crops. The other two three-month periods were established for alfalfa crops. In these conditions, the biomass production is 24.3 ton/(hm^{2}year).

As described above, the amount of copper in the contaminated soil is 672.23 mg_{Cu}/kg_{soil}, and the maximum allowed level of copper in the soil established by the local government regulation is 595 mg_{Cu}/kg_{soil} [39]. Thus, the amount of copper that should be removed is 77.23 mg_{Cu}/kg_{soil}. By considering the BAF values of *B. juncea* and *M. sativa*, the duration of the phytoremediation process using these plants was calculated, and the results are presented in Table 2. In addition, CO_2 fixation for each species was obtained from the literature [45,46] and is also shown in Table 3.

Table 3. Cultivation parameters of the different scenarios.

Parameter	*B. juncea*	*M. sativa*	Rotatory Crop
BAF_{plant}	1.81	3.27	3.27
BAF_{leaves}	1.01	0.86	0.86
Annual crops	2	1	4
Plant biomass [kg/(hm^2·year)]	7472	5249	17970
Leaf biomass [kg/(hm^2·year)]	3736	14151	6334
Total biomass [(ton/(hm^2·year)]	11.20	19.40	24.30
Accumulated Cu [kg_{Cu}/(hm^2·year)]	11.64	19.72	36.21
CO_2 fixation [kg/hm^2·year)]	2781.20	5420.00	4892.24
Years	22	13	7

In order to improve the soil conditions, particularly the porosity, a ploughing step is required. All inventory data for the labour machinery process were adapted from the Gabi Professional 2023 and the Ecoinvent 8.3 databases. As described above, mustard and alfalfa cultivations are enhanced under Mediterranean conditions. In these conditions, a seed rate of 10 kg/hm^2 and 40 kg/hm^2 is assumed for *B. juncea* and *M. sativa*, respectively, according to the literature [44,47].

Table S1 (Supplementary Materials) shows the total amount of seeds. Regarding land fertilisation requirements, the recommendation for soil fertilisation is taken from the literature [27,44,48,49]:

- *B. juncea*: compost (1507 kg/hm^2), EDTA (2806 kg/hm^2), triple superphosphate (150 kg P_2O_5/hm^2), potassium chloride (100 kg K_2O/hm^2) and urea (200 kg/hm^2).
- *M. sativa*: manure (650 kg/hm^2), borax (0.4 $kg/ton_{alfalfa}$), triple superphosphate (7.7 kg $P_2O_5/ton_{alfalfa}$), potassium chloride (7.8 kg $K_2O/ton_{alfalfa}$) and ammonium nitrate (2.7 kg $N/ton_{alfalfa}$).

The calculated values of the fertilisers for each scenario are shown in Table S1.

ii. Conditioning and transport: Biomass must be conditioned to eliminate the soil attached to the biomass. The soil amount was estimated according to the literature [50–52]. For this purpose, a vibration screening is used, and its energy requirement is calculated by simulation using SuperPro Designer 9.5 according to the flowsheet reported elsewhere [32]. The conditioned biomass is then transported to a landfill located 40 km away from the contaminated area. In the case of energy recovery, a cogeneration plant located 79 km from the contaminated area is utilised. Before transportation, the biomass is dried in open air until it reaches a moisture content of up to 20% moisture and then hayed.

iii. Biomass use: As reported by different authors, the environmental sustainability of phytoextraction-based technologies greatly depends on using cultivated biomass. In this sense, two possibilities are evaluated.

   (a) BJ-L, MS-L, RC-L: In these scenarios (see Figure 1), the growth biomass was disposed of as hazardous material in the underground landfill mentioned above; the inventory data are adapted from the Gabi Professional 2023 and the Ecoinvent 8.3 databases.

   (b) BJ-C, MS-C, RC-C: In the cogeneration scenarios (see Figure 1), the harvested biomass was valorised through a combined power and heating system (CPH), simulated using SuperPro Designer 9.5, as reported elsewhere [32]. As explained above, the biomass is transported from the contaminated area to an existing cogeneration plant in which the biomass is stoichiometrically burnt with air, obtaining steam, off-gas and ashes (mainly composed of Cu). This approach is the same as that used in the literature [32]. The molecular formula of *B. juncea* and *M. sativa* was calculated from the elementary analysis obtained from the literature [53,54]. The steam resulting from the process is thereafter expanded in a multistage turbine, yielding electricity and heat with an efficiency of 35% and 50%, respectively [32]. Finally, the ash obtained from the process is transported and disposed of in a landfill for hazardous wastes.

2.3.2. Case 2: Soil Washing

This process was simulated by using SuperPro Designer 9.5 following the scheme reported by Espada et al., 2022 [32], considering a soil treatment capacity of 10 m^3/h. Table S2 (Supplementary Materials) summarises the life cycle inventory data for this case. A scheme of the process, including all the steps involved, is depicted in Figure 1.

i. Excavation and soil transport: The removal of soil contaminated by copper requires the excavation of the soil at a depth of 0.2 m, in this case using an excavator and a skid steer. The soil surface treated was 10,000 m^2, resulting in a soil volume of 2000 m^3.

The distance from the contaminated area to the treatment plant was assumed to be the same as in the landfill scenarios.

ii. Pretreatment and washing: The soil is initially separated using a vibratory wet separator based on its particle size [32], as shown in Table 4.

Table 4. Soil fractions to be treated in Case 2.

Particle	Size (mm)	Percent (%)	Soil Volume (m^3)	Soil to Treat (kg/h)
Gravel	>4	0	0	0
Sand	1.5–4	34	679.8	5.440
	0.075–1.5	38.5	770.2	6160
Silt/Clay	<0.075	27.5	550	4400

The stream consisting of particles sized between 1.5 and 4 mm is transferred to a centrifugation step, where water removal occurs before proceeding to the subsequent washing step. On the other hand, the stream containing particles whose diameter is less than 1.5 mm passes to a hydrocyclone to achieve a more efficient separation. After that, the product stream (particle sizes between 0.075 and 1.5 mm) is conducted to a centrifugation step, while the stream whose diameters do not exceed 0.075 mm is derived to the wastewater treatment unit.

In the washing step, the streams from the aforementioned centrifugation step are mixed and treated with 1M hydrochloric acid (1M of 20% purity) using a soil:acid ratio of 1:3 (by weight) as reported in the literature [55]. The treated soil stream is centrifuged, and the resulting contaminated water stream is directed to the wastewater treatment unit. The treated soil is then used as refilling material.

iii. Wastewater treatment: The stream coming from the washing step is neutralised using sodium hydroxide. This stream and the one coming from the hydrocyclone are mixed, thickened, clarified and centrifuged to remove solid particles. The solid fraction is disposed of in a hazardous landfill (assuming the same distance as in the case of biomass phytoremediation disposal), and the clean water is recycled to the process.

2.3.3. Case 3: Excavation

The inventory data of the different steps for this case are summarised in Table S3 (Supplementary Materials). Figure 1 depicts the steps involved in this treatment.

i. Excavation: The contaminated soil is excavated using an excavator and a mini skid steer. The inventory data of this equipment were adapted from the available process from the Gabi Professional 2023 and Ecoinvent 8.3 databases and adapted to the functional unit.

ii. Landfill deposition: The excavated soil is transported to the landfill by road using a truck. The inventory data of this step were adapted from the databases mentioned above.

iii. Soil refilling: Sand from a quarry located near the contaminated site (28 km) was used to refill the excavated area. This step involves sand charge and its transport using a mini skid steer and a truck.

2.4. Environmental Impact Assessment

In the present work, the environmental impacts were quantified using CML 2001 and EFP methodologies, applying the mid-point approach. The impact categories evaluated are the ones that are usually considered in LCA applied to soil bioremediation [32,56]. In this sense, greenhouse gas emissions (global warming potential category, GWP), acidification and eutrophication potentials (AP and EP, respectively) as well as the toxicity-related impacts of ecotoxicity and human toxicity potentials (ETP and HTP, respectively) were quantified by using the CML 2001–August 2016 methodology. On the other hand, the water use (WU) category was calculated by using the EFP 3.1 methodology. Finally, the direct and indirect primary energy use throughout the life cycle [57] was calculated by the cumulative energy demand (CED).

3. Results and Discussion

The LCA results for all the previously described cases are summarised in Table 5. These results represent the overall values of the different impact categories assessed in this work. In this section, the LCA results for each scenario are discussed by analysing the contribution of the different steps to identify the hot spots in each case. In addition, the scenarios are compared to determine the most environmentally favourable options.

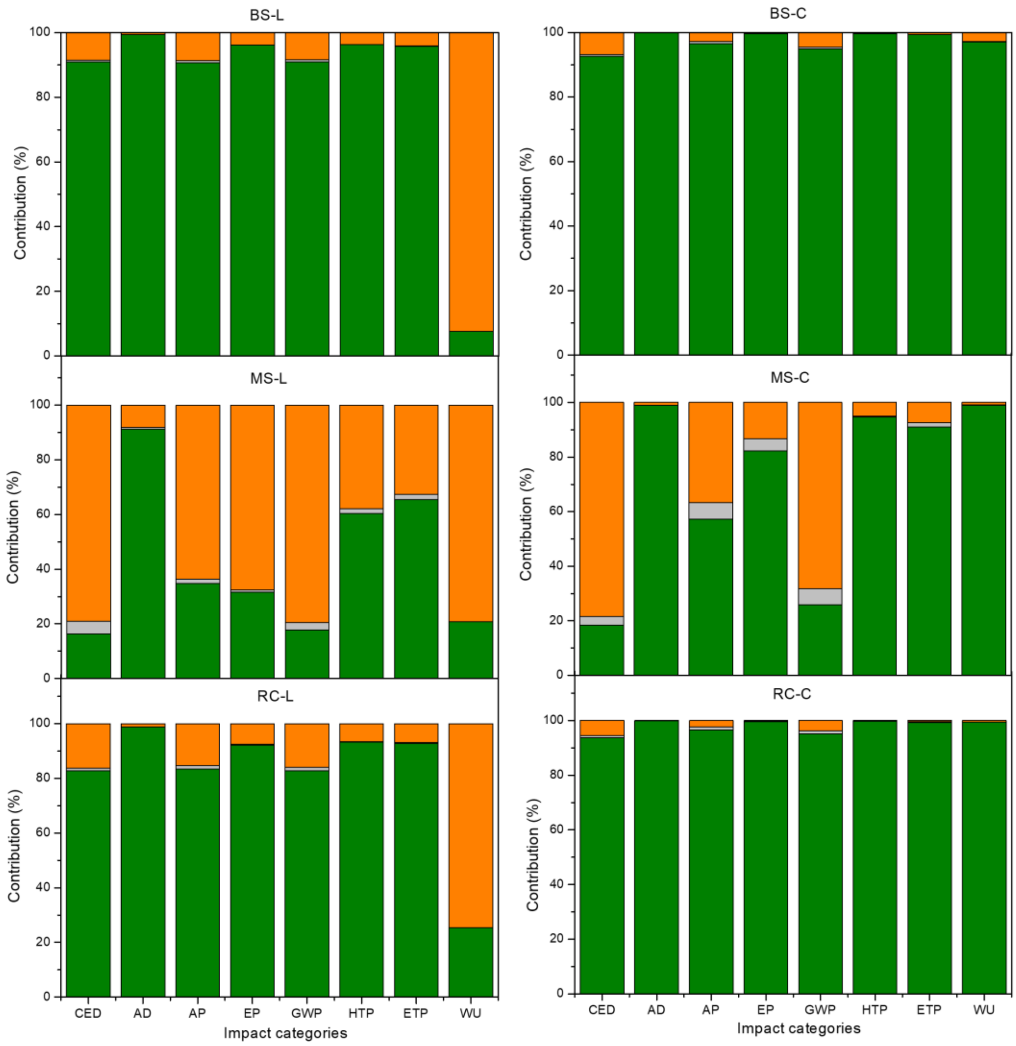
Table 5. Overall impacts for the case studies referred to the FU (1 hm^2 of decontaminated soil).

Impact Category	Case 1						Case 2	Case 3
	BJ-L	**BJ-C**	**MS-L**	**MS-C**	**RC-L**	**RC-C**		
CED (MJ)	$1.3 \cdot 10^7$	$7.5 \cdot 10^6$	$1.4 \cdot 10^6$	-	$7.8 \cdot 10^6$	0	$2.3 \cdot 10^7$	$1.5 \cdot 10^7$
AD (kg Sb-eq)	7.6	7.4	$6.2 \cdot 10^{-1}$	$4.0 \cdot 10^{-1}$	2.8	2.7	8.6	$5.9 \cdot 10^{-1}$
AP (kg SO_2-eq)	$2.1 \cdot 10^3$	$1.7 \cdot 10^3$	$2.8 \cdot 10^2$	-	$8.3 \cdot 10^2$	$5.3 \cdot 10^2$	$2.3 \cdot 10^3$	$2.6 \cdot 10^3$
EP (kg PO_4-eq)	$2.9 \cdot 10^3$	$2.7 \cdot 10^3$	$1.5 \cdot 10^2$	10.9	$1.0 \cdot 10^3$	$9.0 \cdot 10^2$	$8.2 \cdot 10^2$	$1.4 \cdot 10^3$
GWP (kg CO_2-eq)	$5.9 \cdot 10^5$	$3.6 \cdot 10^5$	$6.1 \cdot 10^4$	-	$2.2 \cdot 10^5$	$4.4 \cdot 10^4$	$9.3 \cdot 10^5$	$6.8 \cdot 10^5$
HTP (kg 1,4 DCB-eq) *	$4.5 \cdot 10^5$	$4.1 \cdot 10^5$	$4.4 \cdot 10^4$	-	$1.8 \cdot 10^5$	$1.5 \cdot 10^5$	$1.1 \cdot 10^5$	$2.1 \cdot 10^5$
ETP (kg 1,4 DCB-eq) *	$4.1 \cdot 10^3$	$3.8 \cdot 10^3$	$5.0 \cdot 10^2$	$1.9 \cdot 10^2$	$1.7 \cdot 10^3$	$1.5 \cdot 10^3$	$1.7 \cdot 10^3$	$2.3 \cdot 10^3$
WU (m^3)	$4.3 \cdot 10^6$	$2.3 \cdot 10^5$	$5.9 \cdot 10^3$	$9.0 \cdot 10^5$	$2.0 \cdot 10^4$	$8.8 \cdot 10^5$	$2.2 \cdot 10^7$	$5.1 \cdot 10^7$

* DCB: Dicholorobenzene.

3.1. Phytoremediation

Figure 2 depicts the contribution of each step to the studied impact categories. By analysing the phytoremediation + landfill disposal, it becomes evident that the cultivation and harvesting steps are the largest contributor to most impact categories for *B. juncea* and rotary cultivation (>80%) due to their demanding fertilisation requirements. In the former case, *B. juncea* requires not only NPK fertilisers but also additives such as EDTA in large quantities (5600 kg/hm^2), which generates remarkable impacts due to the substantial energy usage and the emission of hazardous substances during its manufacture. On the contrary, *M. sativa* cultivation contributes less than biomass disposal in most categories (by 60%, except in the AD category) because it can fix nitrogen, thus reducing N-based fertiliser consumption (urea), and this crop does not require EDTA. Regarding the phytoremediation + cogeneration steps, Figure 2 shows a similar trend to the landfill disposal scenarios, except in the case of *M. sativa* where cogeneration has less contribution compared to biomass landfill disposal. In all cases, the biomass conditioning and transport step exhibits the lowest importance in all categories, regardless of the final use of the biomass.



(**a**) (**b**)

Figure 2. Contribution analysis results for phytoremediation-based scenarios combined with (**a**) landfill deposition and (**b**) cogeneration. Green bar: cultivation and harvesting; grey bar: conditioning and transport; orange bar: landfill disposal.

Figure 3 depicts the normalised comparison between all phytoremediation-based scenarios. As can be observed, *B. juncea* is the least desirable option as it presents the highest impact value for each category, regardless of the final use of the biomass. As explained above, the long treatment duration (22 years) as well as the high fertiliser requirements are the main factors affecting the environmental sustainability of this crop for the studied application. By comparing the use of *M. sativa* and rotary cultivation combined with landfill disposal, the former is environmentally better, achieving reductions by 90%, except in WU. It must be noticed that the use of *M. sativa* means double the duration of the treatment compared to rotary cultivation (13 vs. 7 years), but this fact is balanced by the lower impact produced by its cultivation, as explained above. By analysing cogeneration as the final use of the biomass, a similar trend is observed as in the case of landfill disposal, being *M. sativa* and rotary cultivation are the best options, except in the WU category. Their comparative analysis indicates that the former option is clearly superior to the latter option, achieving differences of 30–40% in most categories. Therefore, the obtained results indicate that *M. sativa* is the best option to remove copper from the studied soil regardless of the use of the biomass.

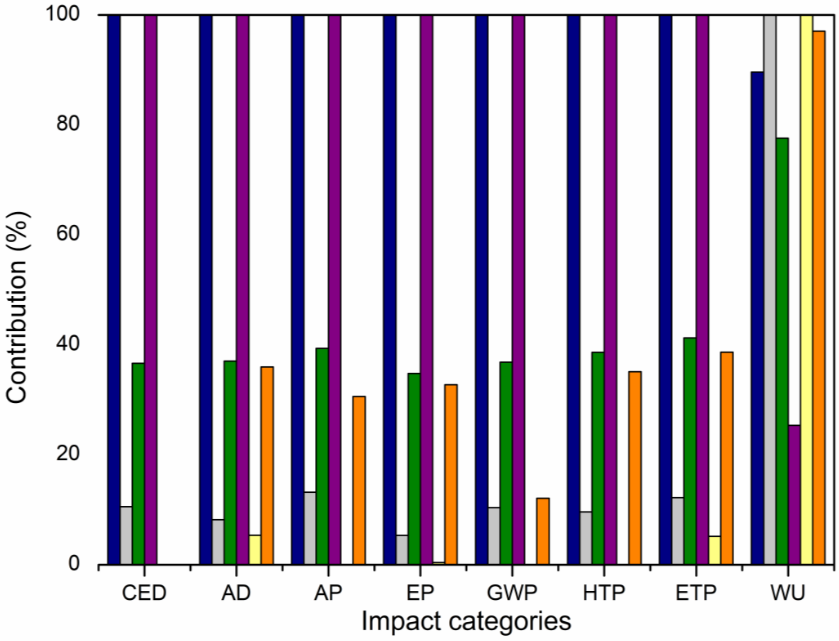


Figure 3. Normalised comparison between phytoremediation scenarios. Blue bar: BS-l; grey bar: MS-L; green bar: RC-L; purple bar: BS-C; yellow bar: MS-C; orange bar: RC-C.

Figure 4 shows the normalised comparison of *M. sativa* combined with landfill deposition or cogeneration. As can be observed, cogeneration is environmentally superior to landfill disposal in all impact categories, which agrees with the results reported by different authors. In this sense, other authors studied the environmental performance of phytoremediation-based treatments to remove Pb from contaminated soil [35]. These authors highlighted the great importance of the biomass use concerning the overall sustainability of the treatment, concluding that phytoremediation without biomass valorisation is not a feasible alternative from an environmental point of view. Furthermore, these authors stated the superiority of using energy recovery as biomass valorisation compared to landfill disposal due to the energy recovery because of the avoided impacts related to heat production. The same conclusions were made by other authors [58], who assessed different scenarios for industrial phytoremediation of a soil contaminated with heavy metals using *C. sativa.* These authors concluded that biomass energy recovery is the most feasible option when using phytoremediation-based treatments. These results were also observed elsewhere [32] for Pb removal from soils using *F. arundinacea*, achieving reductions of 20–80% in all the selected categories.

By considering the impact of reductions achieved by cogeneration over landfill disposal, it can be observed that they ranged between 40 and 100%, which indicates that electricity and heat production is clearly beneficial from an environmental point of view, not only related to energy use (CED, GWP or AP) but also to toxicity-related ones (HTP). The scarcity of impact category results in the literature makes comparing the results shown in this work difficult. Suer et al. (2011) reported impact category results showing the remarkable reductions obtained when combining phytoremediation + energy recovery using *Salix viminalis* to remove BTEX from a soil [59]. Other authors calculated CED for different scenarios, including energy recovery by incineration and anaerobic digestion, ranging from 20 to 35 GJ/hm^2 [58]. These values are lower than those obtained in our work when using landfill disposal but higher than those obtained by the best option using *M. sativa* (Table 2, scenario MS-C). Regarding carbon footprint (GWP) results for arsenic (As), lead (Pb) and Thallium (Tl) removal from a soil using *L. albus*, *B. juncea* and *H. annuus,* some authors reported a value of ~$3 \cdot 10^5$ kg CO_2-eq./hm^2 for biomass landfill disposal, similar to the values for our scenarios including this biomass end use [33]. Concerning scenarios including energy recovery, these authors reported a value of ~$25 \cdot 10^5$ kg CO_2-eq./hm^2, similar to those obtained in our work for the scenarios including cogeneration (Table 4, BJ-C and RC-C) but higher than our best scenario using energy recovery (Table 4, MS-C). Other authors studied the same categories as those analysed in this work, showing that cogeneration was superior to landfill disposal for all impact categories [32]. These comparisons can be used qualitatively to have an idea of the sustainability of the phytoremediation treatments assessed in this work. However, they must be considered with caution, since the conditions of the study (soil characteristics, removed contaminant, etc.) are particular in each case. Despite this and considering these limitations, the sustainability of our best option *M. sativa* + cogeneration (MS-C) is a promising alternative to remove copper from the studied soil.

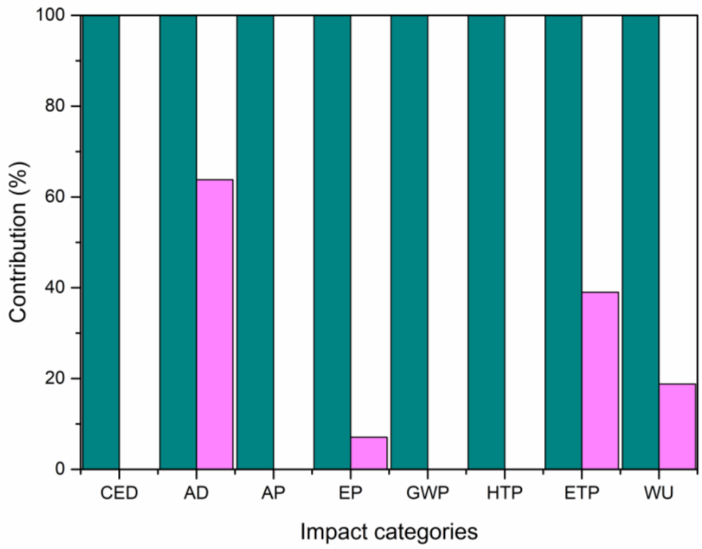


Figure 4. Comparative analysis between the phytoremediation treatments using *M. sativa*. Green bar: MS-L; pink bar: MS-C.

3.2. Soil Washing

Figure 5 shows the relative contribution to the impact categories of the different steps involved in the washing treatment (Case 2). As can be observed, soil landfill disposal is the largest contributor in most categories, except for CED, AD and GWP. This fact is due to the large amount of soil to be disposed of in the security landfill as hazardous material (by 40% of the treated soil). The pretreatment and washing steps are the second contributor in most categories, being the first one for AD (~58%). This contribution is mostly due to using a large amount of hydrochloric acid to solubilise the copper from the contaminated soil. Finally, wastewater treatment contributes 39% to the AD category due to the impacts of using a large amount of sodium hydroxide, whose manufacture and use produces high impacts concerning energy/materials consumption and emissions of hazardous substances. Other authors assessed the carbon footprint of soil washing treatment to remove Pb from contaminated soil, reporting that the most critical contributing steps to the treatment were the transport of soil and wastewater treatment [45]. In addition, the use of HCl in the washing process contributes less than in our case. This is because Pb removal requires a smaller amount of acid than in our case. However, the results reported by these authors are not directly comparable to those obtained in this work since these authors include a previous pretreatment of the soil, which is not included in our work. Nevertheless, the overall carbon footprint value obtained by these authors (~$9 \cdot 10^5$ kgCO_2-eq./hm^2) is similar to that obtained in our case (Table 4, Case 2: $9.3 \cdot 10^5$ kg CO_2-eq./hm^2), despite the different characteristics of the treatment, the soil and the removed metal. Finally, our results agree with the ones reported elsewhere [32] in the sense that the soil to be disposed of and the use of chemicals (HCl and NaOH) contribute largely to most impact categories.

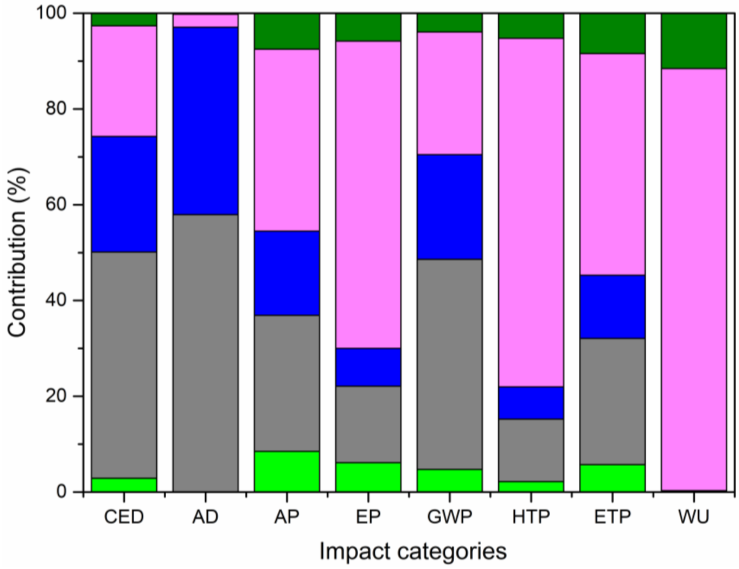


Figure 5. Contribution analysis results for washing treatment (Case 2). Dark green: refilling; pink bar: landfill; blue bar: wastewater; grey bar: pretreatment + washing; green: excavation + transport.

3.3. Soil Excavation

The analysis of the relative contributions to the impact categories associated with the excavation treatment (Case 3) is represented in Figure 6. As inferred, landfill disposal is the most significant contributor (80–95%) to all the impact categories. In this sense, the large amount of contaminated soil (3200 tons) implies a higher consumption of materials and energy for manufacturing containers to store the soil in the secure deposit, resulting in significant contributions of this step across all impact categories. This result agrees well with the work reported elsewhere [59], which analysed phytoremediation (using *Salix viminalis*) + biomass disposal (in a sanitary landfill and in a security deposit), obtaining that the landfill/deposit was the most important contributor (>80%) evaluated for GWP, AP, EP and CED, regardless of the type of landfill. This result is of interest as similar findings are reported by other authors for the treatment of Pb-contaminated soils through excavation [32].

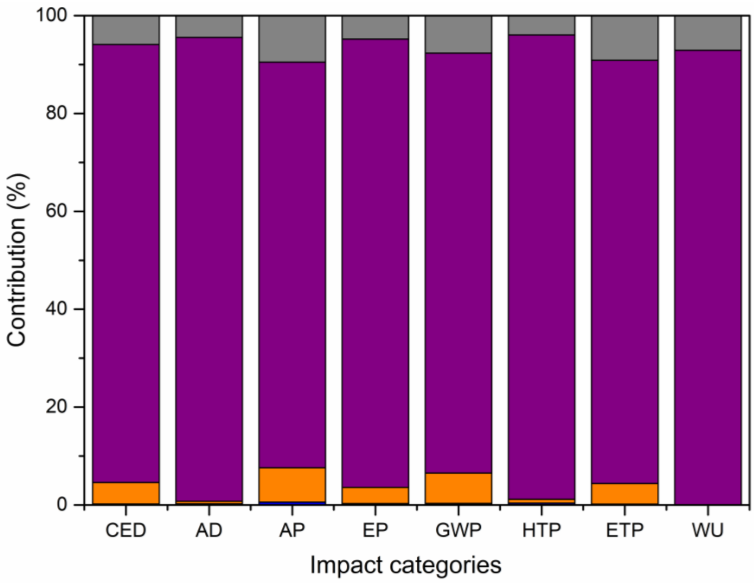


Figure 6. Contribution analysis results for excavation treatment (Case 3). Grey bar: refilling; purple bar: landfill; orange bar: transport; blue bar: excavation.

3.4. Comparative Analysis

Finally, the best phytoremediation-based scenarios (MS-L and MS-C) were compared to the rest of the treatments studied in this work: soil washing (Case 2) and soil excavation (Case 3). Figure 7 depicts the normalised comparison between these treatments from which it can be inferred that the phytoremediation-based scenarios using *M. sativa* (MS-C and MS-L) are clearly superior to the rest from an environmental point of view, achieving reductions between 80 and 100% in the studied categories. Comparing the MS-L and MS-C scenarios, the latter leads to negligible impact values in some categories because energy recovery avoids impacts related to heat and electricity production from biomass. In this sense, the dramatic reduction in energy consumption (CED) and carbon footprint (GWP) must be highlighted. These findings are consistent with other studies examining metal removal from soils. In this sense, other authors [59] reported the comparison of soil excavation and phytoremediation + energy recovery (biofuel), obtaining that the latter was clearly superior for several impact categories (energy consumption, GWP, AP and EP), obtaining reductions of 99% in all cases. Concerning the carbon footprint (GWP) of phytoremediation, soil washing and soil excavation, it is reported in the literature that the former was the most suitable option, achieving reductions >99% and >80% with respect to soil excavation and soil washing treatment [45]. Finally, similar results for most of the impact categories calculated in this work are reported elsewhere [32], revealing phytoremediation (using *F. arundinacea* + biomass cogeneration) as the most suitable option to remove Pb from soil. In this case, it must be noticed that the achieved reductions were lower for most categories (by 75–90%), mainly due to the longer duration of the process (31 vs. 13 years), which implies more demanding requirements that cannot be fulfilled entirely by the energy recovered from biomass.

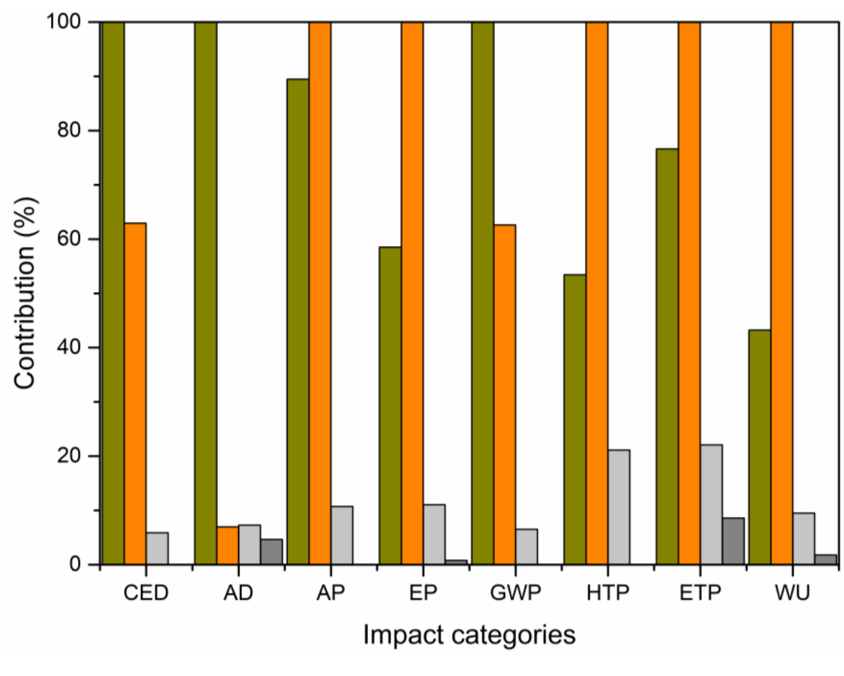


Figure 7. Comparative analysis between the best phytoremediation treatments and the other soil remediation processes (Cases 2 and 3). Dark grey bar: MS-C; light grey bar: MS-L; olive bar: Case 2; orange bar: Case 3.

As inferred from the above discussion, our results agree well with those reported in the literature, despite the differences regarding soil type, plant species and removed metal. These results, although qualitative, indicate the suitability of phytoremediation using *M. sativa* combined with biomass cogeneration to remove copper. In this sense, the results of our work can be a starting point for considering this alternative for further research in the field.

4. Conclusions

Research on environmental sustainability concerning metal removal from soils is ongoing. Nevertheless, systematic studies on this issue are scarce and often applied to a limited number of environmental impacts. In this work, the life cycle assessment (LCA) was applied to environmentally compare phytoremediation-based treatments with other alternatives to remove copper from contaminated soil. For this purpose, different species (*B. juncea*, *M. sativa* and their rotatory crop) were assessed, and they were combined with landfill disposal or cogeneration for biomass use. Experimental and simulation data were used to build the life cycle inventory from which the LCA results were calculated for several impact categories.

The main findings reported in this work are the following:

- *M. sativa* is superior to *B. juncea* and their rotary cultivation as the phytoremediation species from an environmental perspective due to its lower nitrogen fertiliser requirements. This fact balances the longer duration of phytoextraction using *M. sativa* for rotary cultivation, reducing the environmental impact by 30–100% in the analysed categories.
- The contribution of biomass use to the overall impact is more significant in the case of using landfill disposal compared to cogeneration, primarily due to the large amount of biomass to be disposed of as well as the possibility of recovering energy from cogeneration, which reduces environmental impact values.
- The combination of *M. sativa* + cogeneration is clearly superior to the other phytoremediation-based treatments analysed in this work due to the plant's lower fertiliser requirements, its ability to remove copper and the possibility of recovering energy to fulfil most of the process requirements.
- The soil washing treatment involves significant contributions from soil landfill disposal and the use of chemicals (HCl and NaOH required in the process). On the other hand, soil excavation treatment presents soil disposal as the primary contributor to all the studied impacts.
- The combination of *M. sativa* + cogeneration is the option that presents the best environmental performance, achieving reductions up to negligible values in four of eight impact categories (CED, AP, GWP and HTP) due to the impacts avoided by energy production. On the contrary, soil excavation is the least desirable option, followed by the soil washing treatment to remediate the soil studied in this work.

The main limitation of this work is the lack of actual field data on applications of *M. sativa* for copper removal. However, the results reported in this work can be a first step to advancing the research on soil phytoremediation. In this sense, inventory data and LCA results can be used as a benchmark for further studies in this field since they provide the analysis of a wide number of impacts, which is usually scarce in the literature. The main engineering application of our work is to provide LCA results that can help to identify environmental hotspots and to extrapolate our approach to other phytoremediation applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su16062441/s1, Table S1: Inventory data of Case 1 referred to the FU (1 hm^2 of treated soil). Table S2: Inventory data of Case 2 referred to the FU (1 hm^2 of decontaminated soil). Table S3: Inventory data of Case 3 referred to the FU (1 hm^2 of decontaminated soil).

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