

Article

Chelator-Assisted Phytoextraction and Bioenergy Potential of *Brassica napus* L. and *Zea mays* L. on Metal-Contaminated Soils

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Abstract

This study investigates the accumulation potential of *Brassica napus* L. and *Zea mays* L. cultivated on soils contaminated with Zn, Cd, Cu and Pb, using HEDTA—Hydroxyethyl Ethylenediamine Triacetic Acid—to enhance metal mobility. The research addresses a gap in the literature regarding the dual-purpose use of energy crops for assisted phytoextraction and bioenergy recovery. Two pot experiments were conducted on soils of different textures, with HEDTA applied at 2.5 and 5 mmol·kg^{−1}. Metal concentrations in soil and plant tissues were measured, and indices such as the geoaccumulation index (I_{geo}), bioconcentration factors (BCF), translocation factor (TF), metal tolerance index (MTI), crop growth rate (CGR) and higher heating value (HHV) were calculated. Results showed that HEDTA significantly increased Cd and Zn mobility, leading to higher accumulation in rapeseed shoots. Maize demonstrated phytostabilization by retaining metals in roots. Rapeseed biomass exhibited a higher HHV (up to 20.6 MJ·kg^{−1}) and greater carbon and hydrogen content, indicating suitability for thermochemical conversion. Maize, with lower ash content, showed potential for bioethanol production. The findings support the integration of chelate-assisted phytoextraction with energy recovery from biomass.

Keywords: soil pollution; metals; phytoremediation; HEDTA; *Brassica napus* L.; *Zea mays* L.; bioenergy

1. Introduction

Metals are among the most common soil contaminants, occurring in various chemical forms that influence their mobility and bioavailability. The existing regulatory limits for metal concentrations in soil necessitate the development of remediation methods that meet legal, practical, and environmental requirements. Among the available solutions, in situ technologies such as phytoremediation are gaining importance as environmentally friendly approaches to soil decontamination. Additionally, phytoremediation can support carbon sequestration by removing CO₂ from the atmosphere and storing it in the soil in the form of humus, root exudates, soil fauna, and microorganisms [1].

The selection of plants for phytoremediation is based on traits such as rapid growth, high biomass production, root system morphology, and tolerance to elevated metal concentrations [2]. A key factor determining metal uptake by plants is the chemical form of the metals in the substrate, which affects their solubility and availability to plants [3].

Phytoremediation encompasses various techniques [4–6], one of the most frequently studied being phytoextraction, which involves the uptake of metals by roots and their



Academic Editor: José María Ponce-Ortega

Received: 3 October 2025

Revised: 23 December 2025

Accepted: 25 December 2025

Published: 4 January 2026

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accumulation in aboveground tissues [7,8]. Two types of phytoextraction are distinguished: continuous, using hyperaccumulators, and assisted, which employs non-hyperaccumulator species supported by metal-mobilizing agents [9]. Assisted phytoextraction involves increasing metal bioavailability through the application of chelating agents. These agents convert poorly soluble metal forms into plant-available forms, enhancing uptake and translocation to shoots [10–12]. In plants with limited tolerance to high metal concentrations, symptoms of phytotoxicity may occur, such as growth inhibition or premature senescence [13].

The choice of chelating agent depends on the type of contamination, soil properties, cost, and environmental impact [14]. Chelators such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are highly effective in mobilizing metals [15,16]. Luo et al. [11] confirmed the effectiveness of EDTA and ethylenediamine-N,N'-disuccinic acid (EDDS) in assisted phytoextraction, while Ducci et al. [17] highlighted environmental risks associated with their use: EDTA, being non-biodegradable, causes persistent increases in metal solubility, whereas EDDS does not sufficiently enhance bioavailability. The use of chelators carries ecological risks, including increased toxicity to soil microflora and fauna, and the potential migration of soluble metal forms to deeper soil layers and groundwater [18]. Another metal-mobilizing agent, HEDTA, N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetic acid, is a synthetic compound belonging to the group of aminopolycarboxylic acids. Literature reports confirm that HEDTA exhibits the highest selectivity toward Pb in soil [19].

Biomass resulting from phytoremediation may contain metals and organic compounds, posing a risk of introducing contaminants into the food chain. Currently, there is no standardized, recommended method for its neutralization. Its management requires the application of various biochemical (e.g., fermentation, composting), thermochemical (e.g., combustion, pyrolysis), or chemical (e.g., transesterification) methods [20]. Despite these limitations, post-phytoremediation biomass can be used as a renewable energy source. The commonly applied method is combustion with energy recovery. This process involves drying the biomass followed by incineration in dedicated facilities, enabling the recovery of thermal energy. According to Kachel-Jakubowska et al. [21], the calorific value of fresh rapeseed straw ranges from 10.3 to 12.5 MJ·kg⁻¹, reaching up to 15.0 MJ·kg⁻¹ when dried. For maize straw, these values are 5.3–8.2 MJ·kg⁻¹ (fresh) and up to 16.8 MJ·kg⁻¹ (dry). Pre-treatment such as drying or compression reduces transport costs and environmental risks. Controlled combustion allows for energy recovery, and the resulting ash can serve as a bio-ore for metal recovery [22–24]. Currently, biomass accounts for approximately 15–20% of global energy demand, and in developing countries, its share may reach up to one-third of total consumption [25].

The aim of this study was to assess the accumulation capacity of two plant species—spring rapeseed (*Brassica napus* L.) and maize (*Zea mays* L.)—grown on soils contaminated with Zn, Cd, Cu, and Pb following the application of the metal-mobilizing agent HEDTA and to analyze the potential for biomass use.

2. Materials and Methods

2.1. Research Materials

To assess the accumulation capacity of *Brassica napus* L. and *Zea mays* L. on soils contaminated with Zn, Cd, Cu, and Pb, two pot experiments were conducted: A—on very light soil (sandy); and B—on medium-textured soil (loamy).

Both experiments included control soils (S and LS). Soil S was collected from a service-designated area (coordinates: N 51°59'29.42", E 21°13'38.8"), while soil LS was sampled from a forested area (coordinates: N 52°1'40.44", E 20°40'3.13"). The contaminant medium

'c' consisted of sandy soil from a former metallurgical waste disposal site (coordinates: N 50°57'45", E 21°29'52"), characterized by high concentrations of metals. All soils were collected from the topsoil layer (0–0.25 m). Contaminated soils for both experiments were prepared by separately mixing the polluted material (designated as 'c') with the control soils in a 1:7 ratio: with soil S (sandy) in experiment A and soil LS (loamy) in experiment B. In the presentation of results, the contaminated soils were labeled as Sc and LSc. A chelating agent HEDTA was applied to the contaminated soils at two concentrations—2.5 mmol·kg^{−1} (Sc2.5, LSc2.5) and 5 mmol·kg^{−1} (Sc5, LSc5)—at the time of maximum biomass development of both plant species. In total, eight soil combinations were established (S, Sc, Sc2.5, Sc5; LS, LSc, LSc2.5, LSc5), including the control soils, each in three replicates.

2.2. Experimental Design

This study used pot experiments, which play a key role in assessing the potential of plants before their use in field conditions. Results obtained from pot experiments do not always fully reflect field conditions, as yields in pot settings are typically lower. Experiments A and B were conducted in the vegetation hall of the Department of Plant Physiology at the Warsaw University of Life Sciences (SGGW), using two-part Koch-type pots (height: 25 cm, diameter: 22 cm, made to individual order of the SGGW) arranged in a completely randomized design. Each pot was filled with 11 kg of soil. Eight soil combinations were established, each in three replicates, with 24 pots in total (Figure 1).

A	S	Sc	HEDTA	Single dose		– each combination in three replicates – constant soil moisture maintained at 60% of field water capacity – uniform basic NPK fertilization (ammonium nitrate, Polifoska, potassium nitrate) – spring rapeseed (<i>Brassica napus</i> L.) – common maize (<i>Zea mays</i> L.)			
	(sand)	soil contaminated with		(Sc2.5)			(1)	(2)	(3)
	control	metals		Double dose					
	soil			(Sc5)					
B	LS	LSc	HEDTA	Single dose					
	(loam)	soil contaminated with		(LS2.5)		(1)	(2)	(3)	
	control	metals		Double dose					
	soil			(LS5)					

Figure 1. Diagram of pot experiments. Source: Authors' own work.

The first tested plant was *Brassica napus* L., and the next one was *Zea mays* L. The chelating agent HEDTA was applied to the soil at the point of maximum biomass development of both plants. The doses corresponded to 40 and 80 mol·ha^{−1}. Combinations without HEDTA addition were designated as Sc and LSc. Throughout the entire vegetation period, constant soil moisture was maintained at 60% of field water capacity, and uniform NPK fertilization was applied: 0.39 g N, 0.13 g P₂O₅, and 0.26 g K₂O per pot, which is equivalent to 102 kg N, 34 kg P₂O₅, and 68 kg K₂O per hectare. In the experiment, the following were applied per pot: 0.98 g of ammonium nitrate, 0.29 g of Polifoska, and 0.23 g of potassium nitrate, all produced by Grupa Azoty in Puławy, Poland.

2.3. Tested Plants

In pot experiments, two plant species were tested: rapeseed *Brassica napus* L. and common maize *Zea mays* L. (Figure 2). The plant species were selected based on literature data due to their selectivity toward the metals analyzed in this study. According to Luo et al. [26], rapeseed exhibits the highest selectivity for Zn, while Ghnaya et al. [27] indicate that metal stress reduces its yield, with Cd exerting a more pronounced negative effect on growth and development than Zn. In contrast, maize most effectively accumulates Cu, which is primarily stored in the aboveground parts of the plant [26]. Seeds were provided by the Experimental Station in Radzików. Plants were sown in equal quantities, and their

development was monitored according to the Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie (BBCH) scale, Germany [28].



Figure 2. Tested plant: (a) *Brassica napus* L., phase BBCH 21: First side shoot visible; (b) *Zea mays* L., phase BBCH 49: Harvestable vegetative plant parts or vegetatively propagated organs have reached final size. Source: Authors' own work.

Both species were harvested in November at the flowering stage (BBCH 67: End of flowering, most petals have fallen). Plants were collected with roots, cleaned of soil, washed with distilled water, separated into shoots and roots, weighed, dried at 60 °C, and reweighed to determine dry biomass. The biomass was then ground and prepared for further laboratory analyses. The experiments were conducted at a temperature of 20–30 °C, with Photosynthetic Photon Flux Density (PPFD) light intensity maintained at 50–70% [29,30].

2.4. Laboratory Methods for Soil and Plant Material Analysis

Prior to establishing the experiment, selected physical and chemical properties of the collected soils were determined. To ensure high homogeneity of the research material, the samples were dried and sieved through a 2 mm mesh made by Eijkelkamp in Giesbeek, The Netherlands. The following analyses were then performed: particle size distribution using the Casagrande hydrometer method modified by Prószyński according to PTG 2008, Warsaw, Poland; pH in 1 M KCl with pH/Conductivity meter CPC-505 made by Elmetron in Zabrze, Poland [31]; hydrolytic acidity and the content of exchangeable base cations (Ca, Mg) according to the method of Ostrowska et al. [32]; cation exchange capacity (CEC), calculated as the sum of hydrolytic acidity and base cations; organic carbon content [33]; and potassium and sodium concentrations using flame photometry using Jenway PFP7 spectrophotometer made by Jenway/Cole-Parmer in Gransmore Green, Felsted, Dunmow, United Kingdom [34].

After the vegetation period of each tested plant species, soil samples were collected from individual pots. The aim was to assess the accumulation potential of two plant species rapeseed and maize grown on soils contaminated with Zn, Cd, Cu, and Pb following the application of a metal-mobilizing agent (HEDTA). Total metal concentrations were determined in both the soils and the individual plant parts. Samples weighing 0.5 g were digested in a mixture of concentrated HClO₄ and HNO₃ acids in a 3:1 ratio [35]. A Start D microwave digester (made by Milestone in Sorisole, Italy) was used for mineralization. Metal concentrations in the analyzed samples were determined using Atomic Absorption Spectrometry (AAS) for Ca and Mg and Inductively Coupled Plasma Optical Emission

Spectrometry (ICP-OES), for Zn, Cd, Cu and Pb using Thermo Scientific iCAP6500 (made by Thermo Fisher Scientific in Cambridge, United Kingdom) and Varian Axial Vista 720-ES (made by Agilent Technologies in Mulgrave, Australia) spectrometers. For each measurement series, blank samples were prepared in parallel, and their values were considered when calculating results for the actual samples. Method accuracy was verified using the standard addition method.

2.5. Characteristics of Soils and the Chelating Agent HEDTA

The control soils S and LS were characterized by lower metal content and lower sorption capacity compared to the contaminated soils Sc and LSc. Basic physicochemical properties of the soils, such as pH, total organic carbon (TOC), cation exchange capacity (CEC), and concentrations of Ca, Mg, K, and sodium Na, are summarized in Table 1.

Table 1. Physical and chemical properties of control soils (S, LS) and contaminated soils (Sc, LSc).

Soil	TOC	pH KCl	H _h	Ca	Mg	K	Na	CEC
	%							
					cmol(+)·kg ⁻¹			
S	0.11 ± 0.02	8.24	n.d.	2.7 ± 0.3	0.65 ± 0.14	0.08 ± 0.02	0.15 ± 0.03	3.6
LS	0.28 ± 0.03	5.72	1.8	8.6 ± 1.0	0.82 ± 0.11	0.09 ± 0.02	0.14 ± 0.02	9.7
Sc	3.05 ± 0.11	8.77	n.d.	19.7 ± 3.0	4.54 ± 0.50	0.37 ± 0.09	0.81 ± 0.09	25.4
LSc	3.49 ± 0.15	7.10	0.8	24.3 ± 2.4	5.12 ± 0.82	0.65 ± 0.13	0.84 ± 0.15	30.9

H_h —hydrolytic acidity; TOC—total organic carbon; CEC—cation exchange capacity; n.d.—not detected; S, LS—control soils; Sc, LSc—contaminated soils.

The contaminating medium (not included in Table 1) was characterized by an alkaline reaction (pH 8.85), a high organic carbon content (5.20%), and a high cation exchange capacity ($33.6 \text{ cmol}(+)\cdot\text{kg}^{-1}$), as well as a high degree of saturation of the sorption complex with exchangeable base cations, among which calcium ions had the largest share ($25.1 \text{ cmol}(+)\cdot\text{kg}^{-1}$).

To assess the degree of contamination in the control soils (S, LS) and contaminated soils (Sc, LSc), total concentrations of Zn, Cd, Cu, and Pb were determined (Table 2). The results were compared with the permissible values specified for the surface soil layer (0–25 cm) in the regulation [36], taking into account four land-use categories: residential (I), agricultural (II), forest (III), and industrial (IV).

Table 2. Total content of metals in control soils (S, LS) and contaminated soils (Sc, LSc).

Soil	Zn	Cd	Cu	Pb
	$\text{mg}\cdot\text{kg}^{-1}$			
S	61.4 ± 1.5	<det.	19.1 ± 0.9	14.2 ± 0.7
LS	67.3 ± 1.7	0.61 ± 0.08	30.8 ± 1.5	20.8 ± 1.0
Sc	1152 ± 28	9.1 ± 0.8	189 ± 9	798 ± 39
LSc	893 ± 22	8.2 ± 0.7	220 ± 11	817 ± 41

<det.—below the lower limit of detection ($\text{Cd} < 0.5 \text{ mg}\cdot\text{kg}^{-1}$); S, LS—control soils; Sc, LSc—contaminated soils.

Soils S and Sc were classified as subgroup II-1 (very light soils), whereas LS and LSc were classified as subgroup II-3 (medium soils). No exceedances of permissible values were found in the control soils for any of the analyzed metals. However, in soils Sc and LSc, exceedances for Zn, Cd, Cu and Pb were recorded relative to the limits established for the respective land-use categories:

Residential land: Zn—500 mg·kg^{−1}, Cd—2 mg·kg^{−1}, Cu and Pb—200 mg·kg^{−1}.
 Agricultural land: Zn—300 mg·kg^{−1}, Cd—2 mg·kg^{−1}, Cu and Pb—100 mg·kg^{−1} (light soils);
 Zn—1000 mg·kg^{−1}, Cd—5 mg·kg^{−1}, Cu—300 mg·kg^{−1}, Pb—500 mg·kg^{−1} (heavy soils).
 Forest land: Zn—1000 mg·kg^{−1}, Cd—10 mg·kg^{−1}, Cu—300 mg·kg^{−1}, Pb—500 mg·kg^{−1}.
 Industrial land: Zn—2000 mg·kg^{−1}, Cd—15 mg·kg^{−1}, Cu and Pb—600 mg·kg^{−1}.

In the experiments, HEDTA was used as a chelating agent that forms complexes with metal ions. Parameters: molecular weight 278.26 g·mol^{−1}, CAS number 150-39-0, powder form, pH range 7.0–10.0, product by Sigma-Aldrich Chemie GmbH, in Germany [37].

2.6. Computational Methods and Statistical Analysis of Results

Assessing the total metal content in soil is a key step in analyzing the efficiency of assisted phytoextraction, particularly in the context of applying chelating agents such as HEDTA. In this study, concentrations of Zn, Cd, Cu, and Pb were measured in soils from experiment A (very light soil) and experiment B (medium soil), both in control samples and in combinations with HEDTA applied at two dosage levels. The obtained values were compared with the permissible limits specified in the regulation [36], which defines four land use categories: residential (I), agricultural (II), forest (III), and industrial (IV). Based on this comparison, the degree of soil contamination and the potential environmental risk were assessed.

Additionally, to determine the degree of soil enrichment with metals compared to the geochemical background, the geoaccumulation index (Igeo) was calculated using Müller's formula [38], with the average upper continental crust values adopted as the background [39]. In this case, Igeo values allow for the assessment not only of the contamination level but also of the increased phytoavailability of metals following the application of HEDTA. According to the classification by Qing et al. [40], Igeo is divided into seven classes, ranging from no contamination (class 0) to extreme contamination (class 6):

- Class 0—no contamination (Igeo ≤ 0);
- Class 1—slight to moderate contamination (0 < Igeo ≤ 1);
- Class 2—moderate contamination (1 < Igeo ≤ 2);
- Class 3—moderate to heavy contamination (2 < Igeo ≤ 3);
- Class 4—heavy contamination (3 < Igeo ≤ 4);
- Class 5—heavy to extreme contamination (4 < Igeo ≤ 5);
- Class 6—extreme contamination (Igeo > 5).

To assess the ability of plants to uptake metals, the classification proposed by Ma et al. [41] was applied, dividing species into:

- Excluder plants bioconcentration factors (BCF_s < 1):
 - ≤0.01: no accumulation;
 - <0.01–0.1: low accumulation;
 - <0.1–1: moderate accumulation.
- Accumulators (BCF_s = 1–10):
 - >1: high accumulation.
- Hyperaccumulators (BCF_s > 10).

Based on the obtained values, both rapeseed and maize grown on control and contaminated soils were classified as excluder plants.

Pollution factors (Cf) were also calculated using Equation (1) [42]:

$$Cf = \frac{M}{X} \quad (1)$$

where M is the concentration of the metal under analysis and X is the amount of a normalizer element.

Potential environmental risk (RI) is calculated using Equation (2) [42], which allows for the assessment of pollution intensity and its impact on the environment:

$$RI = \sum (Tr^i \times Cf^i) \quad (2)$$

where Tr^i denotes an element's biological toxicity response factor.

To determine the energy efficiency of plant biomass management, the higher heating value (HHV) was calculated using the equation proposed by Jigisha Parikh et al. [43] (Equation (3)):

$$HHV_{\text{fuel}} = 0.3491z_C + 1.1783z_H - 0.1034z_O - 0.0151z_N + 0.1005z_S - 0.0211z_A \quad (3)$$

where z_C is the percentage mass of carbon in fuel; z_H is the percentage mass of hydrogen in fuel; z_O is the percentage mass of oxygen in fuel; z_N is the percentage mass of nitrogen in fuel; z_S is the percentage mass of sulfur in fuel; and z_A is percentage mass of ash in fuel.

The translocation factor was calculated according to Equation (4):

$$TF = \frac{C_s}{C_r} \quad (4)$$

where C_s is the concentration of metal in plant shoots and C_r is the concentration of metal in plant roots [44].

The crop growth rate (CGR) represents the rate of plant biomass increase (Equation (5)):

$$CGR = \frac{dw_2 - dw_1}{p \times (t_2 - t_1)} \quad (5)$$

where dw_1 and dw_2 are the dry weights taken at two separate times represented by t_1 and t_2 , and p is the area of land used for planting.

The metal tolerance index (MTI) represents the relative growth rate of plants exposed to different levels of metal contamination. To enable fair comparison, a modified metal tolerance index is applied by introducing a concentration factor (CF) that reflects the phytotoxicity threshold of the metal (Equation (6)):

$$MTI = \frac{CGR_{\text{sample}}}{CGR_{\text{control}}} \times CF \quad (6)$$

where CGR_{sample} is the plant growth rate under stress, CGR_{control} is the plant growth rate from the control sample, and CF is the concentration factor for each metal.

To assess the impact of HEDTA on metal content in soil and plants, a one-way analysis of variance (ANOVA) was applied [45,46]. Mean comparisons were performed using Fisher's Least Significant Difference (LSD) post hoc test, and statistically significant differences were marked with letters (a, b, c . . .) [47]. All results presented in the tables and figures are mean values from three replicates. Standard deviation was calculated for these mean values (based on three replicates).

Graphical presentation of the results was prepared using Microsoft® Excel® (Microsoft 365, version 2408), and statistical analyses were conducted using the Analysis ToolPak add-in (made by Microsoft Corporation, in Redmond, Washington, United States).

3. Results

3.1. Total Concentrations of Metals in Soil

To evaluate the effectiveness of assisted phytoextraction using HEDTA, total concentrations of metals (Zn, Cd, Cu, and Pb) were determined in soils from experiments A and B (Table 3).

Table 3. Total content of metals in soils [mg·kg^{−1} d.m.] and Igeo.

Plant/Soil		Zn		Igeo	Cd		Igeo	Cu		Igeo	Pb		Igeo		
A	Brassica napus L.	S	56.2	±1.4d	−0.9	0.80	±0.07d	2.5	18.3	±0.9d	−1.0	5.06	±0.25d	−2.6	
		Sc	1107	±27a	3.4	8.62	±0.78a	5.9	121	±6a	1.7	752	±38a	4.7	
		Sc2.5	734	±18b	2.8	5.35	±0.49b	5.2	93.1	±4.7b	1.3	754	±38a	4.7	
		Sc5	611	±15c	2.5	4.63	±0.43c	5.0	52.6	±2.6c	0.5	599	±30b	4.3	
B		LS	59.1	±1.5d	−0.8	0.65	±0.06d	2.1	28.7	±1.4c	−0.4	16.8	±0.8d	−0.8	
		LSc	822	±21a	2.9	7.08	±0.65a	5.6	198	±10a	2.4	802	±40a	4.7	
		LSc2.5	526	±13c	2.3	7.56	±0.68a	5.7	164	±8a	2.1	747	±37b	4.6	
		LSc5	414	±10c	2.0	5.87	±0.53c	5.3	121	±6b	1.7	614	±31bc	4.4	
A		Zea mays L.	S	48.7	±1.2d	−1.1	0.78	±0.07d	2.4	15.6	±0.8d	−1.3	3.25	±0.16c	−3.2
			Sc	1023	±25a	3.3	8.09	±0.74a	5.8	101	±5a	1.4	703	±35a	4.6
			Sc2.5	497	±12c	2.2	4.34	±0.40bc	4.9	67.6	±3.4b	0.9	739	±37a	4.6
			Sc5	472	±12c	2.1	3.71	±0.34c	4.7	36.2	±1.8c	−0.1	556	±28b	4.2
B			LS	55.8	±1.4d	−0.9	0.61	±0.05c	2.1	24.1	±1.2b	−0.6	11.7	±0.6d	−1.4
			LSc	753	±19a	2.8	6.47	±0.59a	5.5	162	±8a	2.1	760	±38a	4.7
			LSc2.5	415	±10bc	2.0	6.63	±0.61a	5.5	130	±7a	1.8	664	±33a	4.5
			LSc5	295	±7c	1.5	4.38	±0.39b	4.9	74.5	±3.7b	1.0	532	±27b	4.2

S, LS—control soils; Sc, LSc—contaminated soils; Sc2.5, LSc2.5—contaminated soils with a single HEDTA dose; Sc5, LSc5—contaminated soils with a double HEDTA dose; letters a, b, c, and d indicate significant differences between means at the 0.05 level according to Fisher's LSD post hoc test.

Zn was present at the highest concentration among the analyzed metals. In Sc and LSc soils, the permissible limits for residential and agricultural land were exceeded, while the threshold for industrial areas (2000 mg·kg^{−1}) was not surpassed. The application of HEDTA increased Zn mobility in the soil, resulting in enhanced phytoavailability, particularly in treatments with the double dose. This allowed these soils to be classified into lower Igeo classes (2–3). It is worth emphasizing that Zn is among the metals most easily mobilized by metal-chelating agents. This relationship is also confirmed by other studies [48].

High concentrations of Cd were found in Sc and LSc soils, exceeding the permissible limits for residential and agricultural areas (2 mg·kg^{−1}). In treatments with HEDTA, Cd content was lower especially with the double dose—yet still above the acceptable levels for agricultural land. The Igeo values for Cd in most cases indicated contamination classes 5–6.

The Cu content in uncontaminated control soils was low and did not exceed any regulatory limits. In Sc and LSc soils, exceedances were recorded for agricultural land (100 mg·kg^{−1}), but not for other land categories. The application of HEDTA, especially at a double dose, significantly reduced Cu concentrations, resulting in lower Igeo values from class 3 in LSc soil to class 0 in Sc5 soil. These results indicate increased Cu mobilization in the soil and, consequently, enhanced phytoavailability of this metal following HEDTA application.

The highest level of contamination was observed for Pb, particularly in Sc and LSc soils, where its concentration exceeded the permissible limits for all land use categories except industrial areas. The Igeo values for Pb in the years 2020–2021 indicated contamination class 5. These results suggest limited mobility of this metal in the soil environment.

In summary, the application of HEDTA increased the mobility and phytoavailability of metals in the soil, resulting in a reduction in their total concentrations—particularly for Zn, Cd, and Cu. Soils treated with the double dose of HEDTA exhibited the lowest Igeo values. The obtained results indicate that the application of assisted phytoextraction significantly increases the efficiency of metal removal from soil compared to phytoextraction without additives. Moreover, the selection of species characterized by high biomass production enables not only effective soil remediation but also the proper management of contaminated biomass, for example, through its use in energy or industrial processes, which helps reduce the risk of secondary environmental contamination.

3.2. Environmental Risk Indicators

Environmental risk assessment in the context of metal presence in soil is a key component in evaluating the effectiveness of remediation processes. This study employed two indicators: the contamination factor (Cf) and the potential environmental risk index (RI), both calculated based on the total concentrations of Zn, Cd, Cu, and Pb after each vegetation cycle. Detailed Cf and RI values for individual metals and soil combinations are presented in Table 4.

Table 4. Values of contamination factor (Cf) and environmental risk index (RI) calculated for soil combinations after harvest of *Brassica napus* L. and *Zea mays* L.

Plant/Soil		Zn		Cd		Cu		Pb		
		Cf	RI	Cf	RI	Cf	RI	Cf	RI	
A	Brassica napus L.	S	0.3	56	0.8	24	0.4	92	0.1	25
		Sc	6.3	1107	8.6	259	2.4	605	10.7	3760
		Sc2.5	4.2	734	5.4	161	1.9	466	10.8	3770
		Sc5	3.5	611	4.6	139	1.1	263	8.6	2995
B	Brassica napus L.	LS	0.3	59	0.7	20	0.6	144	0.2	84
		LSc	4.7	822	7.1	212	4.0	990	11.5	4010
		LSc2.5	3.0	526	7.6	227	3.3	820	10.7	3735
		LSc5	2.4	414	5.9	176	2.4	605	8.8	3070
A	Zea mays L.	S	0.3	49	0.8	24	0.3	78	0.0	16
		Sc	5.8	1023	8.1	243	2.0	500	10.0	3515
		Sc2.5	2.8	497	4.3	130	1.4	338	10.6	3695
		Sc5	2.7	472	3.7	111	0.7	181	7.9	2780
B	Zea mays L.	LS	0.3	56	0.6	18	0.5	121	0.2	59
		LSc	4.3	753	6.5	194	3.2	810	10.9	3800
		LSc2.5	2.4	415	6.6	199	2.6	650	9.5	3320
		LSc5	1.7	295	4.4	131	1.5	373	7.6	2660
Cf	Cf ≤ 1 low contamination		1 < Cf ≤ 3 moderate contamination		3 < Cf ≤ 6 significant contamination		Cf > 6 very significant contamination			
RI	RI < 150, low risk		150 ≤ RI < 300 moderate risk		300 ≤ RI < 600 significant risk		600 ≤ RI high risk			

S, LS—control soils; Sc, LSc—contaminated soils; Sc2.5, LSc2.5—contaminated soils with a single HEDTA dose; Sc5, LSc5—contaminated soils with a double HEDTA dose.

Cf values allow for the assessment of soil contamination levels by individual metals, while RI accounts for the metal's toxicity and its environmental impact.

In control soils (S, LS), all metals showed low contamination levels (Cf ≤ 1) and low environmental risk (RI < 150), confirming their neutral character and lack of environmental

threat. In contaminated soils (Sc, LSc) and in combinations with HEDTA, significant contamination was observed particularly for Cd and Pb where Cf often exceeded 6 and RI reached values above 3000, classifying these soils as high environmental risk.

The application of HEDTA, especially at the double dose, contributed to a reduction in Cf and RI values across most soil combinations. For Zn and Cu, a shift was observed from the class of significant contamination to moderate or low contamination, indicating effective mobilization and partial removal of these metals by the studied plants. For Cd and Pb, despite a clear reduction in concentrations, RI values remained high due to their strong toxicity and persistence in the soil environment.

A comparison of results between the tested plants, rapeseed and maize, revealed a downward trend in both Cf and RI values. This effect was more pronounced in loam soil (experiment B), which can be attributed to its higher sorption capacity and ability to buffer contaminants.

It is important to emphasize that consistently high RI values for Pb across all soil combinations, regardless of the applied HEDTA dose, highlight the need for caution when managing biomass from areas heavily contaminated with this metal in energy recovery processes.

3.3. Metal Content in the Organs of *Brassica napus* L. and *Zea mays* L.

The analysis of Zn, Cd, Cu, and Pb concentrations in the shoots and root tissues of *Brassica napus* L. and *Zea mays* L. enables the evaluation of their capacity for metal accumulation and the identification of potential biomass management pathways in environmental and energy-related contexts. Plants cultivated on control soils (S and LS) exhibited low metal concentrations in both organs (Figures 3 and 4).

Rapeseed exhibited a clear ability to accumulate metals in its shoots, particularly Zn and Cu. On control soils, the sequence of metal uptake was as follows: roots Zn > Pb > Cu > Cd; shoots Zn > Cu > Pb > Cd.

On contaminated soils (Sc, LSc), this pattern was similar, except for LSc soil, where the shoot sequence was: Zn > Cu > Pb > Cd. The application of HEDTA at both doses significantly increased metal uptake, especially into the shoots, which is beneficial from the perspective of phytoextraction. An exception was observed for Cd and Pb in Sc2.5 soil, where their concentrations were higher in the roots. This may indicate limited translocation of these metals at the lower HEDTA dose.

Analysis of variance (ANOVA) revealed significant differences in the concentrations of Zn, Cd, Cu, and Pb in shoots and roots of *Brassica napus* L. and *Zea mays* L., depending on soil type, degree of metal contamination, and the application of HEDTA. The greatest differences occurred between treatments with HEDTA (Sc2.5, Sc5, LSc2.5, LSc5) and contaminated soils without chelator (Sc, LSc), confirming its strong effect on metal mobility. The effect was particularly evident in sandy soil, where metal concentrations in shoots of rapeseed increased several dozen times compared to contaminated soils without chelator.

High concentrations of Zn and Cu in the shoots of rapeseed following HEDTA application indicate effective metal mobilization and translocation. These observations are further supported by translocation factor (TF) values greater than 1. At the same time, the presence of Cd and Pb in the aboveground biomass limits its suitability for consumption and fodder use, directing it toward industrial applications.

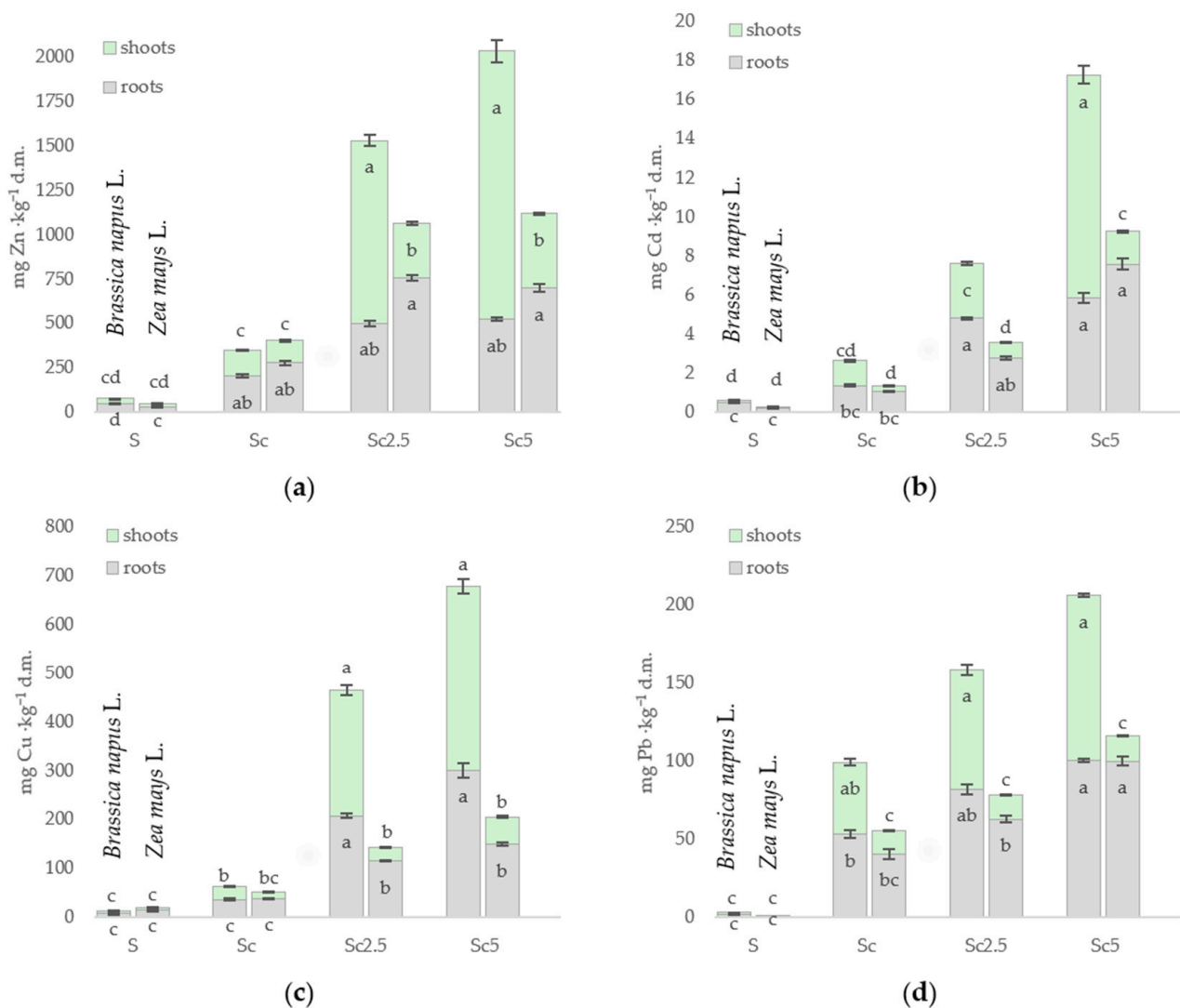


Figure 3. Metal content in shoots and root tissues of rapeseed and maize on sandy soil: (a) Zn; (b) Cd; (c) Zn; (d) Pb; S—control soil; Sc—contaminated soil; Sc2.5—contaminated soil with a single HEDTA dose; Sc5—contaminated soil with a double HEDTA dose; letters a, b, c, and d indicate significant differences between means at the 0.05 level according to Fisher's LSD post hoc test.

Maize exhibited a different accumulation profile. On both control and contaminated soils, the dominant uptake sequence was: Zn > Cu > Pb > Cd. Unlike rapeseed, metals were primarily accumulated in the roots, regardless of the HEDTA dose, indicating its phytostabilization potential. The addition of HEDTA enhanced metal uptake, particularly in the roots, with a stronger effect observed at the double dose.

Low TF values for maize (TF < 1) confirm limited translocation of metals to the shoots. From a bioenergetic perspective, such metal localization may be beneficial in the case of biomass fermentation, where the presence of metals in the shoots can negatively affect the fermentative microflora.

For control soils (S and LS), the aboveground parts of rapeseed and maize met the requirements for consumption use. In contaminated soils (Sc and LSc), the permissible levels of Zn, Cd, Cu, and Pb for consumption and fodder applications were exceeded, particularly following HEDTA application.

Following HEDTA application, regardless of the dose, the shoots of rapeseed and maize qualified exclusively for industrial use. An exception was maize grown in Sc2.5 soil, where the Cu content remained within the permissible range for fodder applications. At

the double HEDTA dose (Sc5, LSc5), Cu also exceeded this threshold, classifying the plant for industrial use.

High calorific value, efficient metal translocation, and industrial suitability indicate that *Brassica napus* L. can be effectively used in phytoextraction processes for metal removal from degraded soils, while simultaneously enabling energy recovery from biomass. Its ability to efficiently uptake and translocate metals, combined with the high energy value of its biomass, makes it an attractive component in circular economy systems that integrate soil remediation with renewable energy production. In contrast, *Zea mays* L., due to its capacity to stabilize metals in the roots and its lower ash content, may be suitable for fermentative bioethanol production or as a protective crop preventing contaminant migration.

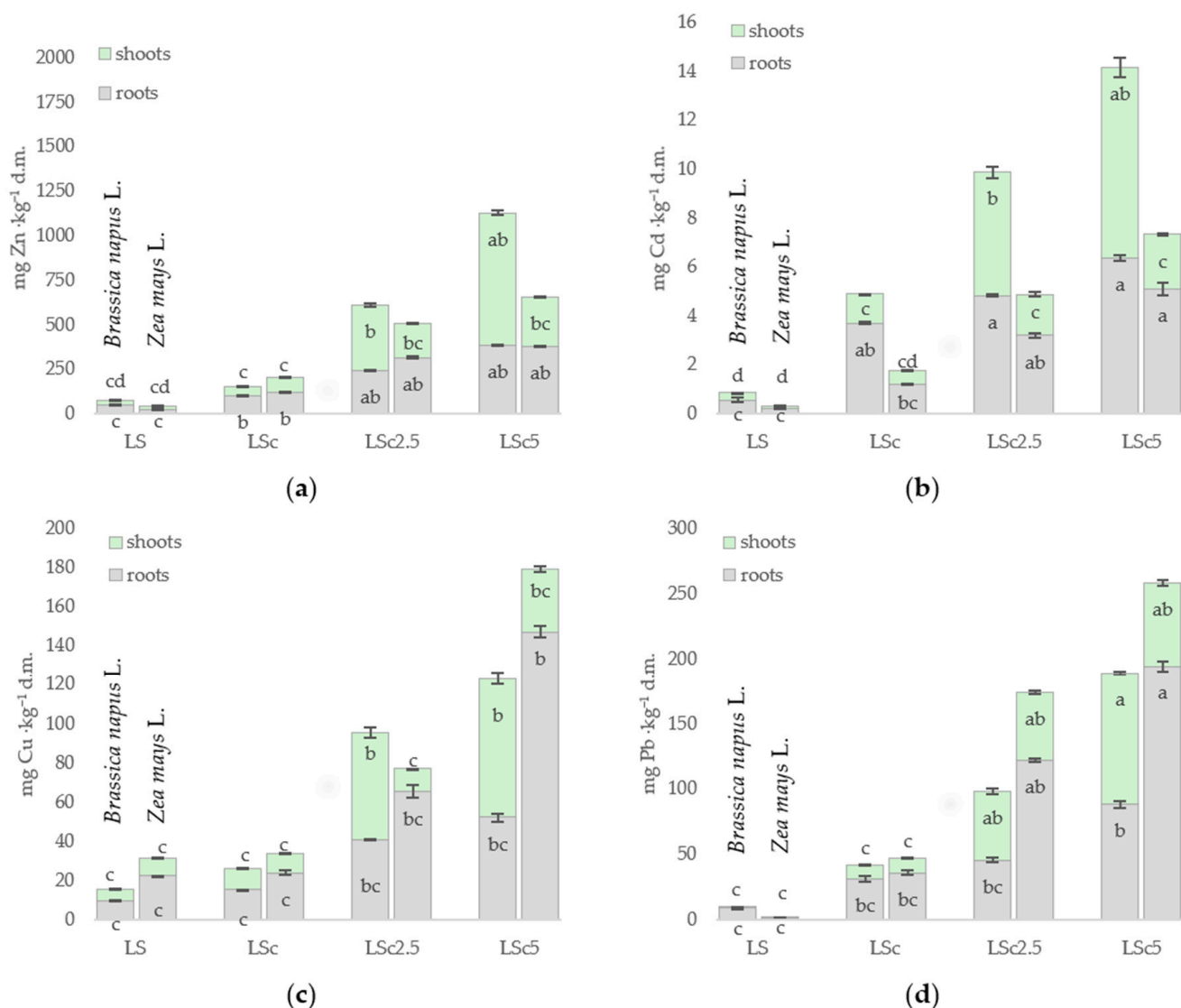


Figure 4. Metal content in shoots and root tissues of rapeseed and maize on loamy soil: (a) Zn; (b) Cd; (c) Zn; (d) Pb; LS—control soil; LSc—contaminated soil; LSc2.5—contaminated soil with a single HEDTA dose; LSc5—contaminated soil with a double HEDTA dose; letters a, b, c, and d indicate significant differences between means at the 0.05 level according to Fisher's LSD post hoc test.

3.4. Bioconcentration and Translocation Factors

To assess the impact of soil type (very light—experiment A; medium—experiment B) combined with HEDTA application, an analysis was conducted on the efficiency of metal uptake and translocation by *Brassica napus* L. and *Zea mays* L.

Bioconcentration factors were determined separately for roots (BCF_r) and shoots (BCF_s), as well as the translocation factor (TF), which defines the plant's ability to transport metals from roots to shoots.

- BCF_r = metal concentration in roots/metal concentration in soil.
- BCF_s = metal concentration in shoots/metal concentration in soil.
- TF = metal concentration in shoots/metal concentration in roots Equation (4).

High BCF values (>1) indicate the plant's ability to accumulate metals, while TF > 1 reflects effective translocation, which is desirable in phytoextraction processes. TF < 1 suggests metal retention in the roots, typical of phytostabilization [2]. Detailed BCF and TF values for all soil and metal combinations are presented in Table 5.

Table 5. Bioconcentration factors and translocation factors in rapeseed and maize organs in both experiments.

Plant/Soil		Zn			Cd			Cu			Pb			
		BCF_s	BCF_r	TF	BCF_s	BCF_r	TF	BCF_s	BCF_r	TF	BCF_s	BCF_r	TF	
A	<i>Brassica napus</i> L.	S	0.52	0.88	0.59	0.18	0.61	0.30	0.34	0.43	0.79	0.16	0.48	0.34
		Sc	0.13	0.19	0.70	0.15	0.16	0.92	0.23	0.31	0.75	0.06	0.07	0.86
		Sc2.5	1.40	0.68	2.05	0.52	0.90	0.58	2.75	2.24	1.23	0.10	0.11	0.93
		Sc5	2.47	0.86	2.87	2.46	1.27	1.95	7.19	5.72	1.26	0.18	0.17	1.06
B	<i>Brassica napus</i> L.	LS	0.46	0.81	0.57	0.44	0.86	0.51	0.20	0.34	0.59	0.06	0.53	0.11
		LSc	0.06	0.12	0.52	0.17	0.52	0.32	0.06	0.08	0.72	0.01	0.04	0.35
		LSc2.5	0.70	0.46	1.53	0.67	0.64	1.05	0.33	0.25	1.34	0.07	0.06	1.15
		LSc5	1.80	0.92	1.95	1.33	1.08	1.23	0.59	0.43	1.36	0.16	0.14	1.14
A	<i>Zea mays</i> L.	S	0.43	0.62	0.69	0.08	0.28	0.28	0.35	0.95	0.37	0.04	0.09	0.42
		Sc	0.12	0.27	0.45	0.04	0.13	0.29	0.12	0.40	0.31	0.02	0.06	0.36
		Sc2.5	0.62	1.53	0.40	0.19	0.64	0.30	0.42	1.72	0.24	0.02	0.09	0.25
		Sc5	0.89	1.48	0.60	0.45	2.05	0.22	1.53	4.15	0.37	0.03	0.18	0.16
B	<i>Zea mays</i> L.	LS	0.32	0.42	0.77	0.16	0.37	0.43	0.38	0.93	0.41	0.03	0.09	0.28
		LSc	0.11	0.16	0.65	0.08	0.19	0.45	0.06	0.15	0.41	0.02	0.05	0.32
		LSc2.5	0.46	0.76	0.61	0.25	0.48	0.53	0.09	0.50	0.18	0.08	0.18	0.42
		LSc5	0.95	1.28	0.74	0.51	1.16	0.44	0.43	1.97	0.22	0.12	0.37	0.33
TF		≤1—no translocation to shoots						>1—translocation to shoots						
BCF ≤0.01—no accumulation				<0.01–0.1—weak level of accumulation			<0.1–1—medium level of accumulation				>1—high level of accumulation			

S, LS—control soils; Sc, LSc—contaminated soils; Sc2.5, LSc2.5—contaminated soils with a single HEDTA dose; Sc5, LSc5—contaminated soils with a double HEDTA dose.

Rapeseed exhibited clearly higher BCF values in both roots and shoots compared to maize. On control and contaminated soils without HEDTA addition, BCF values were low or moderate (BCF < 1), indicating limited accumulation. Following HEDTA application—particularly at the double dose—an increase in BCF above 1 was observed for Zn, Cu, and Cd in the shoots, and for Cu and Cd in the roots, confirming HEDTA's effectiveness in metal mobilization. In experiment B (medium soil), rapeseed showed particularly high accumulation of Cd and Zn in the shoots (BCF_s > 1.8). These results highlight its potential as a phytoextractive species on medium and heavy soils. TF values for rapeseed exceeded 1 in most HEDTA-treated combinations, indicating efficient metal transport to the shoots.

Maize demonstrated the ability to accumulate Zn, Cd, and Cu in the root zone. Lower BCF values were recorded in the shoots, while in the roots, particularly following HEDTA application, BCF values exceeded 1. TF values for maize were below 1 in all combinations, confirming limited metal translocation and its potential for phytostabilization.

In medium soil (experiment B), maize exhibited the highest root bioconcentration factors (BCF_r) for Cu (4.15) and Cd (2.05) in combination with the double HEDTA dose. This indicates a strong capacity for metal accumulation in the root zone. Low translocation factor (TF) values (<0.5) for all metals point to limited transport to the shoots. From an alternative perspective, this may represent a beneficial strategy for minimizing the risk of secondary contamination.

Rapeseed, due to its high BCF_s and TF values, demonstrates potential as a phytoextractive species, particularly under conditions of enhanced metal mobilization. Maize, characterized by dominant root accumulation and low translocation, serves a stabilizing function by limiting metal migration within the soil profile.

The results indicate that plant species selection, soil texture, and chelating agent dosage significantly influence the mechanisms of metal uptake and translocation. From a bioenergetic standpoint, rapeseed may be utilized for energy recovery from metal-contaminated biomass, while maize may serve as a protective crop with potential for fermentative biomass processing under reduced environmental risk.

3.5. Plant Yield

Table 6 presents the fresh and dry biomass yield of shoots and roots of rapeseed (*Brassica napus* L.) and maize (*Zea mays* L.) grown on very light (A) and medium (B) soils, considering the presence of metals and the application of the chelating agent (HEDTA) at different doses.

Table 6. Yield of fresh and dry mass of rapeseed and maize.

Plant/Soil		Shoot Fresh Mass Yield		Fresh Root Mass Yield		Shoot Dry Mass Yield		Dry Root Mass Yield	
		g Per Pot	kg·ha ⁻¹	g Per Pot	kg·ha ⁻¹	g Per Pot	kg·ha ⁻¹	g Per Pot	kg·ha ⁻¹
A	<i>Brassica napus</i> L.	S	11.5 ± 0.4c	3032	2.24 ± 0.1c	597	10.6 ± 0.1c	2786	2.08 ± 0.1c
		Sc	9.7 ± 0.4c	2550	9.28 ± 0.3a	2433	8.9 ± 0.3c	2344	8.48 ± 0.2a
		Sc2.5	10.3 ± 0.2c	2726	9.76 ± 0.5a	2563	9.5 ± 0.4c	2506	8.96 ± 0.4a
		Sc5	3.0 ± 0.1d	779	2.08 ± 0.1c	551	2.7 ± 0.1d	716	1.92 ± 0.1c
B	<i>Brassica napus</i> L.	LS	4.7 ± 0.2d	1216	3.64 ± 0.2b	945	4.3 ± 0.2d	1118	3.25 ± 0.1b
		LSc	3.7 ± 0.1d	969	3.50 ± 0.2b	918	3.4 ± 0.1d	891	3.20 ± 0.1b
		LSc2.5	20.9 ± 0.3b	5503	4.68 ± 0.2b	1229	19.2 ± 0.6b	5058	4.28 ± 0.1b
		LSc5	26.7 ± 0.7b	7016	4.95 ± 0.2b	1305	24.5 ± 0.6b	6449	4.55 ± 0.1b
A	<i>Zea mays</i> L.	S	39.2 ± 1.9a	10,316	1.37 ± 0.1c	361	36.0 ± 0.9a	9482	1.26 ± 0.1c
		Sc	23.5 ± 0.8b	6181	1.04 ± 0.1c	276	21.6 ± 0.5b	5681	0.96 ± 0.1c
		Sc2.5	22.5 ± 0.7b	5909	1.55 ± 0.1c	407	20.7 ± 0.9b	5431	1.41 ± 0.1c
		Sc5	19.8 ± 0.9b	5206	1.59 ± 0.1c	421	18.2 ± 0.8b	4785	1.48 ± 0.1c
B	<i>Zea mays</i> L.	LS	48.3 ± 0.9a	12,703	1.68 ± 0.1c	442	44.2 ± 0.5a	11,676	1.54 ± 0.1c
		LSc	37.6 ± 1.4a	9894	1.04 ± 0.1c	273	34.4 ± 0.4a	9094	0.95 ± 0.1c
		LSc2.5	59.0 ± 1.2a	15,520	1.93 ± 0.1c	512	54.3 ± 2.6a	14,265	1.79 ± 0.1c
		LSc5	62.9 ± 2.7a	16,568	1.09 ± 0.1c	284	58.0 ± 2.4a	15,228	0.98 ± 0.1c

S, LS—control soils; Sc, LSc—contaminated soils; Sc2.5, LSc2.5—contaminated soils with a single HEDTA dose; Sc5, LSc5—contaminated soils with a double HEDTA dose; letters a, b, c, and d indicate significant differences between means at the 0.05 level according to Fisher's LSD post hoc test.

Maize produced significantly higher yields than rapeseed, especially on medium soil (B), where the application of HEDTA in soil B (LSc5) resulted in up to 15,228 kg·ha⁻¹ of shoots. Rapeseed, on the other hand, showed the greatest biomass increase also in soil B (LSc5), reaching 6449 kg·ha⁻¹ of shoots. These results indicate that both soil texture and the HEDTA dose have a substantial impact on plant growth efficiency.

3.6. Management of Plant Biomass

Biofuels derived from plant-based raw materials represent a key component of sustainable energy development strategies. They can be directly used for heat and electricity generation, as well as converted into liquid fuels, making them particularly attractive in the transport sector, which still relies predominantly on fossil-based liquid fuels. Biomass-based fuels, such as biodiesel produced via the Fischer–Tropsch process, can be used in conventional diesel engines without requiring any modifications, further enhancing their practical relevance [49,50].

A wide range of plant species is used globally for biofuel production, including maize, wheat, barley, sugarcane, rapeseed, oil palm, soybean, sugar beet, potato, and sunflower. Rapeseed plays a particularly important role in the European biofuel sector, accounting for as much as 79% of all crops designated for biodiesel production in the European Union in 2008. At that time, the EU was the world leader in biodiesel production, responsible for 60% of global output in 2007. In the context of growing demand for renewable energy sources, energy crops used for biofuel production are gaining increasing importance [51,52].

The evaluation of indicators such as higher heating value (HHV), crop growth rate (CGR), metal tolerance index (MTI), and yield index (YI) enables assessment of their potential for energy and remediation applications. Tables 7 and 8 present a comparison of the energetic and physiological properties of two plant species: *Brassica napus* L. and *Zea mays* L., which are among the most used feedstocks for biodiesel and bioethanol production.

Table 7. Values of HHV for *Brassica napus* L. and *Zea mays* L.

Plant	C %	H %	O %	N %	S %	Ash %	HHV MJ·kg ^{−1}	HHV * MJ·kg ^{−1}
<i>Brassica napus</i> L.	48.9	6.1	34.0	2.7	0.53	7.3	20.6	21.0–25.2
<i>Zea mays</i> L.	45.7	5.7	41.5	0.61	0.08	6.0	18.2	15.3–18.8

* Based on [53] records.

Table 8. Values of CGR and MTI for *Brassica napus* L. and *Zea mays* L.

Plant/Soil		CGR	MTI _{Zn}	MTI _{Cd}	MTI _{Cu}	MTI _{Pb}	
A	Brassica napus L.	S	0.7	-	-	-	
		Sc	0.7	671	915	257	1140
		Sc2.5	0.5	287	367	128	738
		Sc5	0.2	82	109	25	201
B		LS	0.2	-	-	-	-
		LSc	0.8	2133	3215	1798	5202
		LSc2.5	2.7	4583	11,526	5001	16,270
		LSc5	3.1	4180	10,371	4276	15,498
A	Zea mays L.	S	3.1	-	-	-	-
		Sc	1.9	353	489	121	607
		Sc2.5	1.7	158	242	75	588
		Sc5	1.4	125	173	34	369
B		LS	6.4	-	-	-	-
		LSc	6.1	409	616	308	1033
		LSc2.5	3.6	135	376	148	539
		LSc5	4.4	116	301	103	523

S, LS—control soils; Sc, LSc—contaminated soils; Sc2.5, LSc2.5—contaminated soils with a single HEDTA dose; Sc5, LSc5—contaminated soils with a double HEDTA dose.

Table 7 presents data on the elemental composition of biomass and its higher heating value (HHV), which is a key parameter in determining the energy potential of a given feedstock. Rapeseed contains more carbon (48.9%) than maize (45.7%). These results directly translate into a higher heating value. A high hydrogen content (6.1% in rapeseed) also supports combustion efficiency, as hydrogen is a high-energy component of biomass. Maize contains as much as 41.5% oxygen, which lowers the heating value, since oxygen does not contribute to energy generation during combustion and reduces the energy efficiency of biomass. Higher nitrogen (2.7%) and sulfur (0.53%) content in rapeseed compared to maize may lead to NO_x and SO_x emissions during combustion. Therefore, despite its higher energy value, rapeseed may require additional flue gas cleaning systems. Maize has a lower ash content (6%) than rapeseed (7.3%), resulting in fewer combustion residues and reduced risk of deposit formation in energy installations. Rapeseed reaches a heating value of $20.6 \text{ MJ}\cdot\text{kg}^{-1}$, and according to [53], even up to $25.2 \text{ MJ}\cdot\text{kg}^{-1}$, making it a highly efficient energy feedstock. Maize has an HHV of $18.2 \text{ MJ}\cdot\text{kg}^{-1}$, which is considerably lower but still sufficient for bioenergy production, especially in the form of bioethanol.

Table 8 presents indicators of growth efficiency and metal tolerance: YI (yield index), CGR (crop growth rate), and MTI (metal tolerance index for Zn, Cd, Cu, and Pb) for rapeseed and maize cultivated on different soil types, considering metal contamination and the addition of HEDTA. This data compilation enables a comprehensive assessment of both species' potential as feedstocks for biofuel production, considering both their energy value and their ability to grow under environmental stress conditions.

Brassica napus L. exhibits significantly higher metal tolerance than *Zea mays* L., especially in loam soil with HEDTA addition. The use of HEDTA in loam soil markedly increases YI, CGR, and MTI indices.

These results confirm the effectiveness of HEDTA in enhancing plant growth under stress conditions related to metal content in soil. Maize achieves a high CGR under control conditions; however, its low MTI values may pose a limitation for its use in the phytoremediation of highly contaminated soils.

4. Discussion

In this study, a synthetic chelating agent HEDTA, belonging to the aminopolycarboxylic group, was used. It exhibits high selectivity toward Pb [19,54]. The application of HEDTA at two doses (2.5 and $5 \text{ mmol}\cdot\text{kg}^{-1}$) contributed to increased bioavailability of Zn, Cd, and Cu. The increased bioavailability of Zn, Cd, and Cu after the application of HEDTA can be explained by its strong chelating properties. HEDTA forms stable complexes with metal cations through nitrogen and oxygen atoms, reducing their adsorption onto soil particles such as Fe/Mn oxides and clay minerals. This process enhances the solubility and mobility of metals in the soil solution, making them more accessible to plants. Moreover, HEDTA competes with ligands such as humic substances, promoting the desorption of metals from soil surfaces. The stability of HEDTA–metal complexes over a wide pH range further supports their sustained availability during phytoextraction. However, excessive doses of the chelate may increase the risk of metal leaching; therefore, appropriate dosage selection is necessary [55]. The effectiveness of this compound has been confirmed in previous studies [56,57]. Soil texture and pH are key factors influencing metal mobility. The soils used in the experiments (A—very light soil, B—medium soil) were characterized by alkaline pH, which, according to the literature, limits the mobility of Pb and Cu. HEDTA application caused a slight decrease in pH, promoting increased metal availability, particularly for Zn and Cd [58].

A slight decrease in soil pH after the application of HEDTA likely increased the solubility and mobility of Zn and Cd due to changes in chemical speciation. At lower pH values, hydrated and carbonate-bound forms of these metals tend to dissociate, which increases the proportion of free ionic forms (Zn^{2+} , Cd^{2+}) and labile complexes that are more bioavailable. In the case of Cu, which forms hydroxyl complexes under neutral conditions, acidification shifts the equilibrium toward soluble forms, although its affinity for organic ligands remains high. pH values strongly influence the distribution of metal species, with Cd being the most sensitive to acidification, followed by Zn and Cu [59,60].

Rapeseed and maize were selected due to their selectivity toward the studied metals and their energy potential. Rapeseed exhibited higher bioconcentration factor (BCF) values in the shoots for Zn, Cd, and Cu, particularly following HEDTA application. These results confirm its suitability for phytoextraction processes [61,62]. Translocation factors ($\text{TF} > 1$) for Zn and Cd indicate efficient transport of metals from roots to shoots, consistent with the findings of Ashraf et al. [63].

Maize exhibited lower BCF values in the shoots, while $\text{BCF} > 1$ for Zn and Cd was recorded in the roots. This pattern of metal accumulation indicates its phytostabilizing nature [64,65]. TF values below 1 for all metals confirm limited translocation, consistent with the findings of Tandy et al. [66] and Zhao et al. [67], who demonstrated that maize retains metals primarily in the root zone.

The Cf and RI indices reported by Li et al. [48] revealed varying levels of soil contamination, depending on the type of metal and the treatment combination applied. The highest Cf and RI values were recorded for Pb, resulting from its high initial concentration and limited mobility. The application of HEDTA contributed to a reduction in contamination levels, particularly for Zn and Cu, as confirmed by the findings of Komárek et al. [68] and Kos et al. [69]. In the case of Pb, despite its low bioavailability to plants, the environmental risk remained high, indicating the need for further remediation efforts. Pb exhibits a strong affinity for Fe/Mn oxides, clay minerals, and organic matter, which results in its immobilization in soil. It forms poorly soluble compounds such as carbonates, phosphates, and sulfides, so the concentration of free Pb^{2+} ions in the soil solution remains very low even with a decrease in pH. Due to its high persistence and toxicity, even small amounts of Pb can pose a threat to groundwater and soil organisms, which justifies the need for remediation strategies aimed at its immobilization or removal [70,71].

Rapeseed demonstrated a clearly higher energy potential than maize. The carbon and hydrogen content in rapeseed biomass translates into a higher heating value, averaging $20.6 \text{ MJ} \cdot \text{kg}^{-1}$ compared to $18.2 \text{ MJ} \cdot \text{kg}^{-1}$ for maize [53]. Maize is characterized by a lower energy value and reduced ash content, which is advantageous in combustion processes.

Biomass obtained from plants grown on contaminated soils can be used for biofuel production, thermal energy generation, and thermochemical processes such as pyrolysis or gasification. Due to its ability to accumulate metals and its high heating value, rapeseed is a particularly attractive feedstock for biomass use on degraded lands [72,73].

In the context of sustainable management of degraded lands, an important development direction is the integration of remediation processes with energy recovery from plant biomass. Plants used in phytoextraction, such as *Brassica napus* L. and *Zea mays* L., can serve a dual function: soil decontamination from metals and provision of energy feedstock. This approach aligns with the principles of the circular economy and decarbonization strategies, promoting resource recovery from biological waste [74,75].

An analysis of the elemental composition of biomass revealed that rapeseed is characterized by higher carbon and hydrogen content and lower oxygen content compared to maize, which translates into a higher heating value. According to data from [53], the heating value of rapeseed can reach up to $25.2 \text{ MJ} \cdot \text{kg}^{-1}$, while for maize it peaks at ap-

proximately $18.8 \text{ MJ} \cdot \text{kg}^{-1}$. However, the higher nitrogen content in rapeseed may lead to increased NO_x emissions during combustion, which should be considered when designing energy systems [76].

The significantly higher ash content in rapeseed compared to maize may affect combustion efficiency and the amount of solid residues. The presence of metals in biomass, particularly Pb and Cd, can result in the emission of toxic compounds during thermochemical processes such as combustion, pyrolysis, or gasification [77]. Therefore, biomass from remediation plants should be directed toward industrial applications, with appropriate emission control and flue gas cleaning systems in place.

Rapeseed biomass, due to its high heating value and fat content, can be used, for example, in biodiesel production and as solid fuel in industrial boilers. Maize, thanks to its lower ash content, is more suitable for anaerobic digestion and bioethanol production [75,78,79].

It is worth noting that the presence of metals in biomass may affect microbial activity in fermentation processes. Therefore, maize grown on contaminated soils should be directed toward technologies with high tolerance to pollutants, such as plasma gasification or fermentation involving adapted microbial communities [67].

In experiment B (medium soil), significantly higher biomass yields were obtained compared to experiment A (very light soil). The highest dry shoots yield for rapeseed was recorded in the LSc5 combination ($6449 \text{ kg} \cdot \text{ha}^{-1}$), while for maize it was in the LSc5 combination ($15,228 \text{ kg} \cdot \text{ha}^{-1}$). The application of HEDTA at the double dose increased rapeseed yield, whereas in the case of maize, an opposite effect was observed likely due to species-specific differences in tolerance to the presence of metals in the soil.

Biomass from plants growing on metal-contaminated soils produces ash with elevated concentrations of Zn, Cu, Pb and Cd after combustion, which necessitates its classification as hazardous waste [80]. Therefore, it should be subjected to metal recovery or stabilization processes. Khare et al. [81] demonstrated that leaching using various acids or mobilizing agents enables efficient metal recovery. Other authors [82,83] emphasize that cement-based stabilization and the binding of metals within mineral structures significantly reduce their mobility and toxicity, allowing for safe disposal. This means that ash can be treated both as a source of secondary raw materials and as waste requiring neutralization.

Metal-contaminated biomass may also be directed to bioethanol production processes. Fermentation and distillation yield bioethanol free of inorganic contaminants, while metals remain in the post-fermentation residue [84–87]. The most rational solution for the post-fermentation mass is its thermal processing, which leads to the concentration of metals in the ash. Begum et al. [88] describe integrated biochemical and thermochemical processes that enable simultaneous recovery of energy and raw materials, whereas Wang et al. [89] indicate that modern biomass combustion technologies within circular economy frameworks allow efficient energy production while limiting emissions.

Such an approach enables full utilization of metal-contaminated biomass: bioethanol as a clean fuel, ash as a source of metals for recovery or stabilization, and energy as an additional outcome of the process. This aligns with the concept of the circular economy, in which waste becomes a resource and the risk of secondary environmental contamination is minimized.

Transferring results obtained under controlled conditions to real (field) conditions primarily requires consideration of environmental factors. Pot experiments are conducted under constant moisture and without climatic variability, whereas in the field there are rainfall events, temperature fluctuations, microbial activity, and heterogeneous soil structure. These factors affect metal mobility and the effectiveness of applied chelators [90]. An important aspect is the risk of metal leaching into groundwater after chelator application, especially during heavy rainfall. Therefore, in practice, it is necessary to apply appropriate

chelator doses and monitor the environment [91]. Research results indicate that rapeseed is more effective in phytoextraction, while maize is better suited for phytostabilization. However, in field conditions, local climate, water availability, and biomass management options must be considered [92,93]. Integrating remediation processes with energy recovery from biomass is feasible but requires technologies that limit metal emissions during combustion, pyrolysis, or gasification [88].

Based on the metal content in aboveground biomass and its energy value, rapeseed and maize grown on contaminated soils qualify for industrial applications. Rapeseed can be used in biofuel production, pellet manufacturing, and as a feedstock for gasification. Maize, due to its lower metal content in aboveground biomass, may be considered for anaerobic digestion and bioethanol production. Research findings indicate that integrating remediation processes with energy recovery from plant biomass represents a promising strategy for managing degraded lands, combining environmental goals with the production of renewable energy sources.

5. Conclusions

1. The application of HEDTA significantly increased metal mobility in the soil, leading to effective accumulation in plants and a reduction in Igeo, Cf, and RI indices. The effect was more pronounced with the double HEDTA dose.
2. Rapeseed demonstrated a clearly higher phytoextraction potential than maize, particularly for Zn, Cd, and Cu, as confirmed by $BCF_s > 1$ and $TF > 1$ values. Maize acted as a phytostabilizing species, retaining metals in the roots.
3. Rapeseed biomass exhibited a higher calorific value (up to $20.6 \text{ MJ} \cdot \text{kg}^{-1}$), making it a more efficient energy resource than maize, which—due to its lower ash content—may be preferred in fermentation processes.
4. YI and MTI indices confirmed rapeseed's high tolerance to metals, especially in loam soil with HEDTA addition. Maize showed a higher growth rate under control conditions, but its tolerance was lower than that of rapeseed.
5. The utility of biomass varied depending on soil conditions and HEDTA application. Rapeseed and maize showed industrial applicability for Zn, Cd, and Pb, while Cu was suitable for feed use (maize, $2.5 \text{ mmol} \cdot \text{kg}^{-1}$ dose) or industrial use ($5 \text{ mmol} \cdot \text{kg}^{-1}$ dose).
6. The results confirm that assisted phytoextraction can be an effective method for remediating metal-contaminated soils while simultaneously providing biomass with high energy potential. Integrating these processes aligns with the goals of sustainable development and energy transition.

Author Contributions: Conceptualization, A.P., D.R., A.K., P.K. and M.W.; methodology, A.P. and D.R.; software, A.P. and D.R.; validation, A.P. and D.R.; formal analysis, A.P., D.R., A.K., P.K. and M.W.; investigation, A.P., D.R. and M.W.; resources, A.P. and D.R.; data curation A.P. and D.R.; writing—original draft preparation, A.P. and D.R.; writing—review and editing, A.P., D.R., A.K., P.K. and M.W.; visualization, A.P. and D.R.; supervision, A.P.; funding acquisition, A.P. and D.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Faculty of Environmental Engineering, Warsaw University of Technology, under the following projects: “Assessment of the effectiveness of metal-mobilizing agents for the remediation of cohesive and non-cohesive soils, with particular emphasis on induced phytoextraction” (Project No. 504/03691/1110/42.000100) and “Determination of the impact of process parameters on the remediation of metal-contaminated soils” (Project No. 504/04465/1110/44.000000).

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed at the corresponding author.

Conflicts of Interest: Author Arkadiusz Kamiński was employed by ORLEN S.A. Author Peter Knosala was employed by the company BHU Umwelttechnik GmbH. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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