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Reagent-Assisted Phytoextraction Potential for Heavy and Critical Metals on a Contaminated Post-Mining Substrate as NBS

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Abstract

Restoring contaminated and degraded land, including post-mining sites, industrial areas, and urban brownfields, is central to sustainable land management, and nature-based solutions (NBSs) such as phytoextraction can combine soil remediation with wider landscape-restoration goals. This screening-stage pot study evaluated how three mobilising agents, potassium iodide (KI), calcium chloride ($CaCl_2$), and ammonium chloride (NH_4Cl), applied at 20, 50, and 80 mg kg^{-1} against a common citric-acid background, affect the uptake and translocation of 27 potentially toxic elements and critical raw materials in *Brassica juncea* and *Cichorium intybus* grown on a met-al-contaminated post-mining substrate from Srednogorie, Bulgaria, which is used as a model of severely degraded technogenic material relevant to industrial and urban brownfield conditions. Bioconcentration and translocation factors were calculated from XRF measurements of the substrate, root, and leaf tissue and examined descriptively with exploratory principal component analysis and clustering, since each combination was one composite sample. Plant species identity, rather than reagent, was the strongest determinant of accumulation: *Brassica juncea* more often retained Y, Sr, Th, and Zn in roots, whereas *C. intybus* translocated Rb, Sr, Pb, and Cu more readily to leaves. KI produced the most distinct profile, increasing root and, at the highest dose, shoot enrichment of V, whereas $CaCl_2$ and NH_4Cl mainly enhanced root retention with limited, non-monotonic effects on shoot transfer. These species- and element-specific strategies indicate screening-stage potential for phytoextraction, pending validation with replicated biomass and yield data.

Keywords: nature-based solutions; urban brownfield restoration; critical raw materials; potentially toxic elements; chemically assisted phytoextraction

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1. Introduction

The restoration of contaminated urban land is increasingly recognised as an important component of sustainable urban development. Brownfields, former industrial areas and other degraded urban sites frequently contain elevated concentrations of potentially toxic elements, which impose long-term constraints on land use and reduce the ecological, social and economic value of urban landscapes. Nature-based solutions (NBSs) provide a framework for addressing these challenges by combining environmental remediation with the recovery of ecosystem functions, maintenance of vegetation cover and broader landscape-restoration objectives.

Conventional remediation methods, including excavation, off-site disposal and physicochemical treatment, are often costly and may substantially disturb soil structure, fertility

and biological functioning, thereby causing long-term impacts on ecosystem processes [1,2]. These limitations have stimulated interest in less disruptive remediation approaches that can be implemented in situ while maintaining or gradually restoring soil and landscape functions. Phytoextraction, defined as the uptake of elements from contaminated soil and their accumulation in harvestable plant tissues, has therefore received considerable attention as a potentially cost-effective and non-destructive alternative to engineering-based remediation [1,3,4]. When integrated into longer-term site management, plant-based remediation may also support revegetation, erosion control and the progressive ecological recovery of degraded land.

In addition to potentially toxic elements, contaminated urban and industrial substrates may contain economically valuable elements associated with critical raw materials (CRMs), including rare earth elements, tungsten, tantalum, indium and gallium. These materials are essential for renewable-energy technologies, electronics and advanced manufacturing, and concerns regarding their secure and sustainable supply are increasing worldwide [5]. The accumulation of such elements in plant tissues may therefore provide a basis for linking remediation with future resource-recovery strategies within a circular-economy framework. However, concentration in plant tissues alone does not demonstrate effective removal from the substrate or economically viable recovery, such an assessment also requires information on plant biomass, total element yield, changes in soil concentrations over time and the management of the harvested material. In the absence of these measurements, plant concentrations and translocation indices should be interpreted primarily as indicators of phytoextraction potential.

Plant species occurring or readily establishing in disturbed habitats may be particularly suitable for nature-based remediation because they can provide vegetation cover while tolerating adverse substrate conditions. *Brassica juncea* and *Cichorium intybus* are promising candidates for chemically assisted phytoextraction due to their capacity to establish themselves on contaminated substrates and accumulate several potentially toxic elements, including Cd, Pb, and Zn, in roots and above-ground tissues [6–8]. The However, these two species, however, may employ contrasting accumulation strategies.: *Brassica* species are frequently characterised by substantial uptake and sequestration in the root system [9], whereas *C. intybus* has demonstrated effective xylem transport and accumulation in leaf tissues, potentially favouring the transfer of selected elements to harvestable above-ground biomass [8,10]. These physiological differences suggest that the species may perform complementary functions, with some elements predominantly retained below ground and others more effectively translocated to shoots [9,10].

The effectiveness of phytoextraction is frequently constrained by the limited bioavailability of elements in soil.: many Many contaminants and potentially valuable elements are strongly associated with mineral surfaces, organic matter, or other rela-tively stable soil fractions and are therefore not readily accessible to plant roots. Con-sequently, elevated total concentrations in soil do not necessarily result in proportion-ally high concentrations in plant tissues [11,12]. Chemical mobilisation has been pro-posed as a means of increasing the soluble or exchangeable element fraction and thereby enhancing plant uptake. Previous studies have shown that amendments can increase the concentrations of selected contaminants in plant tissues relative to un-treated controls [11,13].

Synthetic chelating agents such as EDTA are among the most extensively investigated mobilisation treatments; however, their use raises concerns because strong and persistent metal–chelant complexes may remain mobile beyond the period of active plant uptake, increasing the risk of element transport below the root zone and contamination of groundwater [12]. These environmental trade-offs are particularly relevant when chemically assisted phytoextraction is considered within an NBS framework. An intervention cannot

be regarded as sustainable solely because it employs plants; the benefits of increased element uptake must also be assessed against the risks of leaching, salinisation, phytotoxicity, and adverse effects on soil organisms and vegetation development. This has encouraged the investigation of alternative inorganic salts and less persistent mobilisation treatments that may modify element availability while avoiding some of the limitations associated with conventional synthetic chelants. In addition, low-molecular-weight organic acids are released naturally by plant roots as exudates, where they influence the mobility and uptake of metals in the rhizosphere. Citric acid, one of the most common exudates, was therefore applied uniformly to all pots to reproduce this organic-acid component of root exudation and to examine its influence on element behaviour, while also exemplifying the low-cost, readily biodegradable, and non-persistent amendments favoured over synthetic chelators such as EDTA. Applying it identically to every pot allowed the effects of the three inorganic salts to be assessed against a common, root-exudate-like organic-acid background rather than against untreated substrate.

Despite growing interest in chemically assisted phytoextraction, limited information is available on how alternative mobilisation agents affect a broad range of potentially toxic, rare, and CRM-associated elements in plant species with contrasting accumulation and translocation strategies. In particular, the relative importance of plant identity, reagent type, and application dose remains insufficiently resolved, and increased root accumulation must be distinguished from enhanced transfer to above-ground tissues, because these responses correspond to different remediation functions and harvesting requirements.

The three inorganic reagents were selected so that a single, comparatively simple set of salts could probe several different mechanisms of action on the substrate–soil-solution–plant system while avoiding persistent synthetic chelators. The underlying concept is halide-assisted metal complexation: iodide and chloride are ligands that form soluble complexes with several metals—the principle behind the well-documented induced accumulation of gold [14]—and chloride leaching is widely applied in hydrometallurgy, yet its role in phytoextraction remains comparatively little studied. In addition, calcium chloride is, in addition, a standard reagent for assessing the ex-changeable and readily soluble element fractions [15], so its action can be interpreted in terms of ion exchange and chloride complexation, with the latter shown to increase the solubility and plant uptake of elements such as Cd [16]. Ammonium chloride combines the same chloride effect with an ammonium cation that, through nitrification, can gradually acidify the substrate and further increase the availability of metal cations. Potassium iodide supplies a transiently available iodide together with K^+, an essential plant macronutrient; because part of any response may therefore be associated with K^+ rather than I^-, the iodide effect cannot be attributed to the halide alone. Selecting reagents that share a chloride ligand but differ in their cation (Ca^{2+}, NH_4^+), together with an iodide reagent, allowed these contrasting effects to be compared while monitoring the accompanying changes in pH and the condition of the experimental system were monitored.

The present pilot study therefore evaluated the effects of potassium iodide (KI), calcium chloride ($CaCl_2$), and ammonium chloride (NH_4Cl), applied at three doses, on element uptake and distribution in *B. juncea* and *C. intybus*. The plants were grown on a highly contaminated mine-waste substrate used as a model of severely degraded technogenic material relevant to industrial and urban brownfield conditions. Concen-trations were determined separately in the substrate, roots and leaves, and the resulting bioconcentration and translocation patterns were used to distinguish treatment com-binations associated predominantly with root retention from those favouring transfer to above-ground tissues. Because dry biomass and total element removal were not measured, the study assesses

accumulation and translocation potential are assessed in the study rather than quantitative extraction efficiency.

Based on this objective, four hypotheses were formulated: (i) *B. juncea* and *C. intybus* would exhibit measurable but element-specific accumulation of potentially toxic and CRM-associated elements; (ii) KI, $CaCl_2$, and NH_4Cl would produce ele-ment-specific responses rather than uniform increases in plant uptake; (iii) the two species would differ in the allocation of accumulated elements between roots and above-ground tissues; and (iv) reagent and dose combinations producing increased above-ground accumulation and translocation would indicate greater potential for phytoextraction-oriented management, whereas combinations characterised by root retention would be more consistent with phytostabilisation-oriented strategies. The broader relevance of these contrasting responses to nature-based remediation was evaluated in terms of plant selection, harvesting requirements, and the environmental trade-offs associated with reagent application.

2. Materials and Methods

2.1. Study Site and Substrate Collection

The experimental substrate was collected from a historical waste-rock dump lo-cated in the Srednogorie mining region, Bulgaria. The site (Figure 1) represents post-mining brownfield land formed as a result of former mining activities and is characterised by a strongly disturbed technogenic substrate with limited natural soil development. The surrounding vegetation is dominated by black pine (*Pinus nigra*) plantations, while the geological setting consists predominantly of volcanic rocks and heterogeneous Qua-ternary deposits.

Figure 1. Historical waste-rock dump and post-mining brownfield in the Srednogorie mining region, Bulgaria.

The collected material was characterised by limited soil development, strong ini-tial acidity, and elevated concentrations of several potentially toxic elements. It, and was therefore used as an experimental model of a severely degraded technogenic sub-strate relevant to the restoration of post-mining, industrial, and urban brownfield sites.

Substrate sampling was conducted in February 2026 at an elevation—of 750 m. M, material was collected from a depth of 30–50 cm at 5 points. and the The individual field samples were combined to produce the bulk substrate used in the experiment.

The collected material was transported to the laboratory, air-dried, sieved, and thoroughly homogenised before use.

2.2. Experimental Design and Plant Cultivation

A controlled pot experiment was conducted with common chicory (*Cichorium intybus* L.) and mustard (*Brassica juncea* L.), with 30 pots prepared for each species, giving 60 cultivation units in total. Each pot (13 cm in diameter, 9 cm in height, and 0.5 L in volume) contained 300 g of dried, sieved and homogenised substrate, and substrate moisture was maintained at approximately 60–70% of field capacity throughout cultivation.

Ten treatments were established for each species: an untreated control and KI, $CaCl_2$, and NH_4Cl, each applied at 20, 50, and 80 mg kg^{-1} dry substrate (equivalent to 6, 15 and 24 mg of reagent per pot, respectively). A stepwise, three-level concentration series was used so that any dose-dependence of the response could be tracked and a range identified in which uptake is enhanced without evident phytotoxicity, rather than to maximise mobilisation; the levels were kept low enough to limit salinity stress and to keep reagent inputs compatible with the low-impact character of a nature-based intervention. Each treatment comprised three pots, which were maintained separately during cultivation; the material from the three pots was then pooled before chemical analysis, yielding one composite analytical sample per species × treatment combination.

Before sowing, the substrate was conditioned to correct its strong initial acidity and low nutrient status: each pot was limed with 2.47 g of $Ca(OH)_2$ and fertilised with 2.38 g of YaraMila COMPLEX NPK 12-11-18. Fifteen days after this conditioning, substrate pH had risen from 2.6 to 7.3, after which the plants were established.

All pots, including the controls, received a uniform application of citric acid, which—as one of the principal low-molecular-weight organic acids released by plant roots as exudates—was applied to reproduce this organic-acid component of root exudation in the rhizosphere and to examine its influence on element mobilisation and uptake. It also exemplifies the low-cost, readily biodegradable and non-persistent amendments favoured over persistent synthetic chelators such as EDTA: its carboxylate groups can transiently complex several metals and promote their desorption, while it is rapidly metabolised by soil microorganisms and therefore dissipates quickly from the substrate, limiting prolonged mobility and leaching. Because citric acid was applied identically to every pot, the control-relative responses reported below isolate the additional effect of KI, $CaCl_2$, or NH_4Cl superimposed on this common, root-exudate-like organic-acid background. The design did not include a citric-acid-free control, and rhizosphere-solution samples and element valence states were not determined; therefore, the independent contribution of citric acid and the underlying element speciation cannot be resolved here and are addressed in the Discussion and in the proposed validation design. The citric-acid dose of 1 g kg^{-1} dry substrate (0.30 g per pot) was chosen as a balance between mobilisation and plant safety: on this weakly buffered, sandy substrate, a dose of this order is reported to lower substrate pH from about 7.2–7.3 to about 5.5, sufficient to increase the availability of several metals without causing marked phytotoxicity, whereas higher doses lower pH further and increase mobilisation but also the risks of phytotoxicity and leaching [17–20]. Result of the experiment is presented on Figure 2.

Figure 2. Experimental design involving *Cichorium intybus*, *Brassica juncea* and the applied KI, $CaCl_2$ and NH_4Cl treatments.

2.3. Reagent Application and Sample Coding

The mobilising reagents were applied on 20 May 2026, once the plants were well established and actively growing, by dissolving KI, $CaCl_2$, or NH_4Cl in water and applying the solution to the substrate surface; the control pots received the same volume of water without added reagent. Substrate pH was measured before the subsequent citric-acid application. Citric acid was then applied to carried out on all pots, including the controls, on 3 June 2026 at 1 g kg^{-1} dry substrate (0.30 g per pot). Substrate pH and

electrical conductivity were measured again before the final sampling, and substrate, root and leaf material was collected for elemental analysis on 17 June 2026. The plants were cultivated for approximately two months in total.

Sample numbers 1–10 corresponded to *Cichorium intybus*, whereas numbers 11–20 corresponded to *Brassica juncea*. Within each species, the numbering followed the same treatment sequence: control; KI at 20, 50, and 80 mg kg^{-1}; $CaCl_2$ at 20, 50, and 80 mg kg^{-1}; and NH_4Cl at 20, 50, and 80 mg kg^{-1}.

The sample matrices were coded as follows: S1–S10: were substrate samples from *C. intybus* treatments; S11–S20: were substrate samples from *Brassica juncea* treatments; K1–K10: were root samples from *C. intybus*; K11–K20 were: root samples from *Brassica juncea*; L1–L10: were leaf samples from *C. intybus*; L11–L20 were: leaf samples from *Brassica juncea*.

The control samples received citric acid but no preceding KI, $CaCl_2$, or NH_4Cl treatment.

2.4. Elemental Analysis

The elemental composition of the substrate, root and leaf samples was determined by semi-quantitative energy-dispersive X-ray fluorescence spectrometry (SPECTROSCOUT portable XRF spectrometer, Screening Powders analytical method) at the Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences. Prior to measurement the dried samples were sieved and homogenised, and approximately 8–10 g of prepared material was used for each determination.

Before analysis, all samples were dried, homogenised and prepared according to the instrument requirements.

The analysed elements were Pb, Cu, Cr, Zn, V, Cd, As, Hg, Ba, Zr, Rb, Ce, La, Y, Ga, Ta, W, Sr, Sn, Cs, Ni, Mo, Th, In, Sb, Te and Co.

Values reported below the analytical detection limit were treated as censored observations and were not replaced with zero. Element-specific detection information is provided in Supplementary Table S1.

2.5. Bioconcentration, Translocation and Treatment Response

Bioconcentration and translocation indices were calculated by matching substrate, root and leaf samples with the same numerical code, thus, S1, K1 and L1 represented the corresponding substrate, root and leaf samples from the first *Cichorium intybus* treatment, while S11, K11 and L11 represented the corresponding samples from the first *Brassica juncea* treatment.

Element enrichment in the roots was evaluated using the root bioconcentration factor:

$$BCF_{root} = \frac{C_{root}}{C_{substrate}} \quad (1)$$

where C_{root} is the concentration of the respective element in the root tissue and $C_{substrate}$ is its concentration in the corresponding post-treatment substrate sample.

Element enrichment in the above-ground tissues was evaluated using the shoot bioconcentration factor:

$$BCF_{shoot} = \frac{C_{leaf}}{C_{substrate}} \quad (2)$$

where C_{leaf} is the concentration of the respective element in the leaf tissue.

Root-to-shoot element transfer was evaluated using the translocation factor:

$$TF = \frac{C_{leaf}}{C_{root}} \quad (3)$$

Values of $BCF_{root} > 1$ or $BCF_{shoot} > 1$ indicate that the concentration of the respective element in the plant tissue exceeded that in the corresponding substrate sample, these values were interpreted as indicators of relative tissue enrichment and not as sufficient evidence of hyperaccumulation. Values of $TF > 1$ indicate preferential translocation to the leaves, whereas values those below 1 indicate predominant retention in the roots.

The combined interpretation of the three indices was used to distinguish contrasting element-allocation patterns: high BCF_{root} accompanied by $TF < 1$ was interpreted as predominant root retention, consistent with a phytostabilisation-oriented response, while higher BCF_{shoot} accompanied by $TF > 1$ indicated greater potential for transferring the respective element to harvestable above-ground tissues.

Treatment responses were evaluated relative to the corresponding species-specific control, which received citric acid but no preceding KI, $CaCl_2$ or NH_4Cl treatment. The absolute difference relative to the control was calculated as:

$$\Delta C_{treatment} = C_{treatment} - C_{control} \quad (4)$$

The fold change relative to the control was calculated as:

$$FC = \frac{C_{treatment}}{C_{control}} \quad (5)$$

where $C_{treatment}$ represents the element concentration or calculated index for a given reagent and dose, and $C_{control}$ represents the corresponding value for the same plant species in the control.

The percentage change relative to the control was calculated as:

$$\%\Delta C_{treatment} = \frac{C_{treatment} - C_{control}}{C_{control}} \times 100 \quad (6)$$

For graphical comparison of responses differing substantially in magnitude, fold changes were also expressed on a base-2 logarithmic scale:

$$\log_2 FC = \log_2\left(\frac{C_{treatment}}{C_{control}}\right) \quad (7)$$

A value of $\log_2 FC = 0$ indicates no change relative to the species-specific control, while positive and negative values indicate an increase and decrease, respectively. Thus, values of +1 and −1 correspond to a two-fold increase and a two-fold decrease, respectively.

Control-relative metrics were calculated only when both the treatment and control values were exact, positive numerical values; bound ratios and n.c. entries were excluded from the calculations. No pseudocounts or substitutions were introduced. Because percentage change is mathematically related to FC as $\%\Delta X = (FC - 1) \times 100$, the main text emphasises FC and $\log_2 FC$, while all four metrics are presented in Supplementary Table S3.

Responses across the ordered doses of 20, 50 and 80 mg kg^{-1} were examined separately for each plant species, reagent, element and index. A complete three-dose series was classified as increasing when the index increased successively across all three doses, decreasing when it declined successively, and non-monotonic when neither condition was met. Series containing censored or non-calculable values were excluded from this classification. Because each dose was represented by one composite analytical observation, the dose patterns were interpreted descriptively.

Dry root and shoot biomass was not determined.; therefore, total Total uptake and removal from the substrate could therefore not be calculated. Thise study assesses ele-ment

concentrations, relative tissue enrichment, root retention, root-to-shoot transloca-tion, and control-relative responses rather than total phytoextraction yield.

2.6. Data Analysis

Each plant species × treatment combination was represented by a single composite analytical sample, because material from the three cultivation pots was pooled before chemical analysis. The dataset therefore contained no independent within-treatment replicates, and all analyses were descriptive and exploratory; no inferential statistical tests, confidence intervals, or adjusted p-values were computed. Elemental concentra-tions, BCF_{root}, BCF_{shoot}, TF values, and control-relative fold changes were examined separately for each plant species, reagent, and dose. Responses across the ordered doses of 20, 50, and 80 mg kg^{-1} were compared descriptively: a series was classified as direc-tional when the index increased or decreased successively across all three doses, and as non-linear when its maximum or minimum occurred at the intermediate dose. These dose patterns were not subjected to statistical dose–response testing.

Principal component analysis (PCA) and hierarchical clustering were used to ex-plore multi-element variation within the BCF_{root}, BCF_{shoot}, and TF datasets, with a separate analysis for each index. Treatment combinations were treated as observations and el-ements as variables. Prior to analysis, the data were log-transformed; variables with zero variance, insufficient quantified observations, or unstable ratios were ex-cluded, and the retained variables were centred and scaled to unit variance. Clustering was performed on the z-score-standardised, log-transformed data using Euclidean dis-tances and Ward's minimum-variance linkage, and the results were visualised as heatmaps and dendrograms. Both techniques were used exclusively to identify explor-atory patterns; separation among species, reagents or dose levels was not interpreted as statistical evidence of treatment effects.

Values below the analytical detection limit were treated as censored observations and were not replaced with zero or with an assumed detection-limit value. Ele-ments with insufficient quantitatively determined observations were excluded from ra-tio-based and multivariate analyses.

All calculations and exploratory analyses were performed in R version 4.5.3. Prin-cipal component analysis and associated graphical outputs were generated using the FactoMineR and factoextra packages.

Generative artificial intelligence was used as an assistive tool during manuscript prepa-ration. OpenAI ChatGPT was used to support the structural organisation and language editing of the manuscript and to assist with the preparation of descriptive calculations and visualisations based exclusively on the authors' experimental dataset. The tool was not used to generate experimental data or to make autonomous scientific decisions. All calcu-lations, interpretations, references, and AI-assisted outputs were independently checked, revised, and approved by the authors.

3. Results

3.1. Elemental Concentrations in the Substrate and Plant Tissues

The complete elemental concentrations measured in the substrate, root, and leaf samples are provided in Supplementary Table S1. Each value represents one composite analytical sample corresponding to a specific plant species, reagent and application dose.

The substrate samples contained comparatively high concentrations of Pb, Ba, Zr, Cu, Cr, and Rb. Pb concentrations ranged from 739.7 to 1022 mg kg^{-1} dry weight, while Ba and Zr ranged from 649.1 to 720.1 mg kg^{-1} and from 194.0 to 273.1 mg kg^{-1}, re-spectively. The corresponding ranges for Cu, Cr, and Rb were 173.0–255.5 mg kg^{-1},

161.4–184.4 mg kg^{-1}, and 154.5–171.1 mg kg^{-1}, while Zn and V concentrations ranged from 102.5 to 171.8 mg kg^{-1} and from 62.7 to 83.5 mg kg^{-1}, respectively.

Root and leaf concentrations varied more strongly among plant species and treatments. In *Cichorium intybus*, the highest root concentrations of Pb, Cu and V occurred under KI at 20 mg kg^{-1}, whereas the highest Zn concentration was recorded under NH_4Cl at 50 mg kg^{-1}. In *Brassica juncea*, comparatively high root concentrations of Zn occurred under several $CaCl_2$-, KI- and NH_4Cl-based treatments.

The leaf profiles differed from those observed in the roots: elevated leaf concentrations of V, Sr, Rb, and Zn were recorded in selected treatments, whereas Pb, Cu, Zr, Y, and Th generally remained more concentrated in the roots than in the leaves. The complete concentration profiles for the substrate, roots and leaves are shown in Figure 3 and tabulated in Table S1.

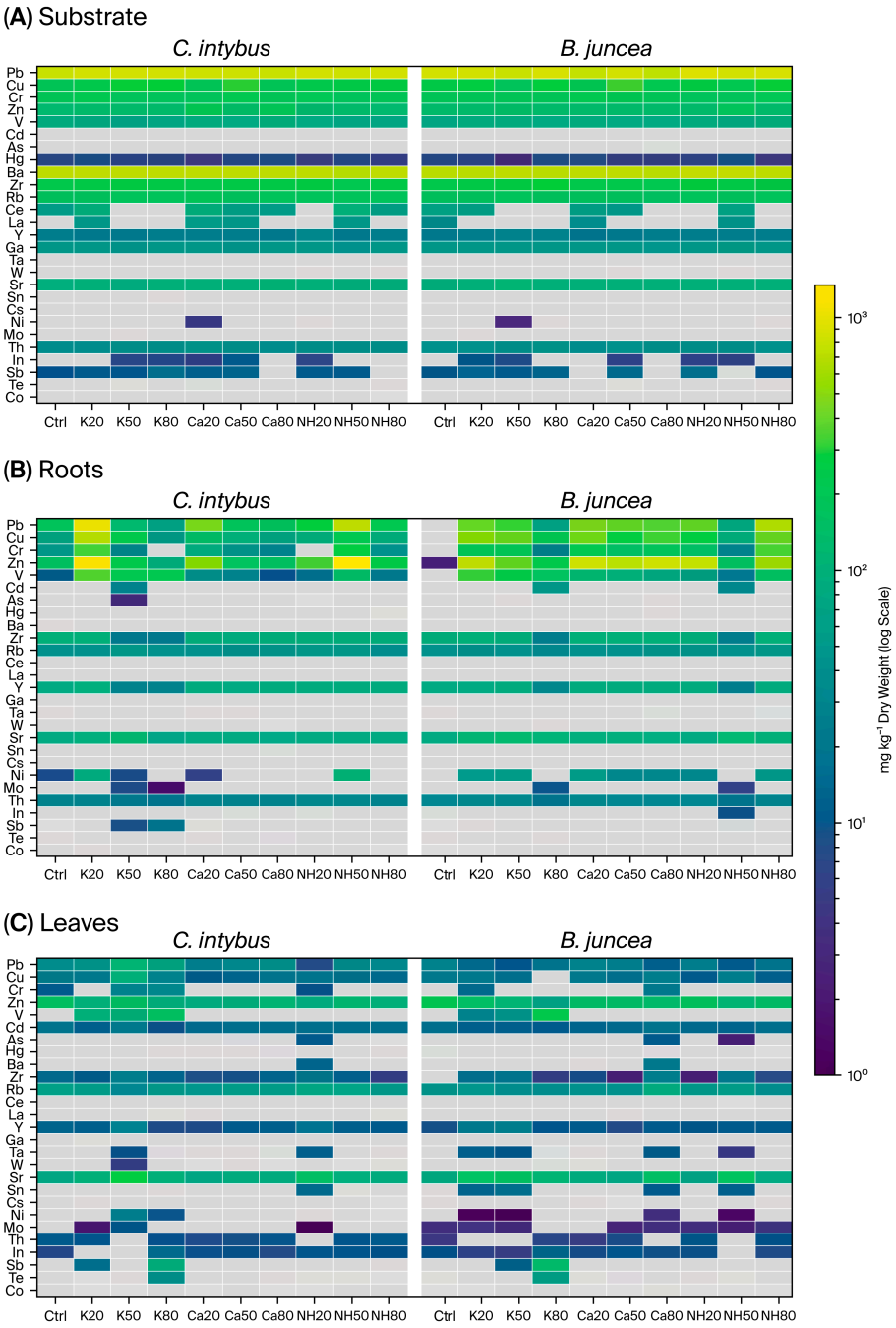

Figure 3. Elemental concentration profiles in the substrate, roots and leaves of *Cichorium intybus* and *Brassica juncea* under the control, KI, $CaCl_2$ and NH_4Cl treatments. Grey cells represent values below the analytical detection limit.

3.2. Availability of Bioconcentration and Translocation Indices

For the 27 analysed elements and 20 treatment combinations, 540 values could theoretically be calculated for each concentration-based index. However, ratios were calculated only when both concentrations required for the respective calculation were quantitatively determined.

Overall, BCF_{root} was calculable for 199 of the 540 possible element–treatment combinations, BCF_{shoot} for 179 combinations and *TF* for 170 combinations; thus-Thus, 548 of the 1620 theoretically possible bioconcentration and translocation coeffi-cients were retained (Table S2).

Complete BCF_{root} datasets covering all 20 treatment combinations were availa-ble for Zn, Zr, Rb, Y, Sr, and Th. Complete BCF_{shoot} coverage was available for Pb, Zn, Rb, Y, and Sr, while complete *TF* coverage was limited to Zn, Rb, Y, and Sr. Pb, Cu, and Zr also had comparatively high coverage, but one or two treatment-specific values could not be calculated.

BCF and *TF* values could not be evaluated systematically for As, Hg, Ce, La, Ga, Ta, W, Sn, Cs, Te, and Co because the relevant concentrations were predominantly below the analytical detection limit. Cd, Ni, Mo, In, and Sb produced only isolated valid ratios and were therefore not used to define general treatment or species patterns.

All individual coefficients, including the number of valid observations for each element, are provided in Supplementary Table S2.

3.3. Root Bioconcentration

Root bioconcentration showed pronounced element-, species- and treatment-specific variation, as summarised in Figure 4.

In *C. intybus*, Zn showed BCF_{root} values above 1 in eight of the ten treatments. The highest Zn BCF_{root} was recorded under NH_4Cl at 50 mg kg^{-1}, reaching 10.76; KI at 20 mg kg^{-1} also resulted in a high Zn BCF_{root} of 8.95.

Y was consistently concentrated in the roots of chicory, with BCF_{root} values above 1 in nine of the ten treatments; the highest value was 4.97 under NH_4Cl at 50 mg kg^{-1}. Most Y values ranged between approximately 2.5 and 4.6, indicating persistent root enrichment across chemically contrasting treatments.

KI at 20 mg kg^{-1} produced the highest root bioconcentration values for several other elements in chicory, including the following:

- Pb: BCF_{root} = 1.15.
- Cu: BCF_{root} = 3.50.
- Cr: BCF_{root} = 1.90.
- V: BCF_{root} = 5.68.

The response was not maintained consistently at the higher KI doses; for example, the BCF_{root} of Cu decreased from 3.50 at 20 mg kg^{-1} to 0.61 at 50 mg kg^{-1} and 0.11 at 80 mg kg^{-1}.

In *Brassica juncea*, Zn also showed substantial root bioconcentration, with BCF_{root} values above 1 in eight of the ten variants. The highest values were recorded under $CaCl_2$ at 20 and 80 mg kg^{-1}, reaching 6.87 and 6.85, respectively, while NH_4Cl at 20 mg kg^{-1} produced a BCF_{root} of 6.19 and KI at 20 mg kg^{-1} produced a value of 5.93.

Y was enriched in *Brassica* roots in nine of the ten variants. The highest Y BCF_root was 5.67 under $CaCl_2$ at 20 mg kg^{-1}, followed by 5.05 under $CaCl_2$ at 50 mg kg^{-1}.

Cu showed BCF_{root} values above 1 in seven of the nine calculable *Brassica* variants, and the highest value was 2.21 under KI at 20 mg kg^{-1}. The highest Cr BCF_{root}, 2.19, was recorded under NH_4Cl at 80 mg kg^{-1}, while V reached a maximum BCF_{root} of 4.08 under KI at 20 mg kg^{-1}.

Pb did not show systematic root enrichment in *Brassica juncea*; all calculable BCF_{root} values were below 1.

Columns represent the individual control and reagent–dose combinations. The reference value BCF_{root} = 1 distinguishes concentrations below and above those measured in the corresponding substrate.

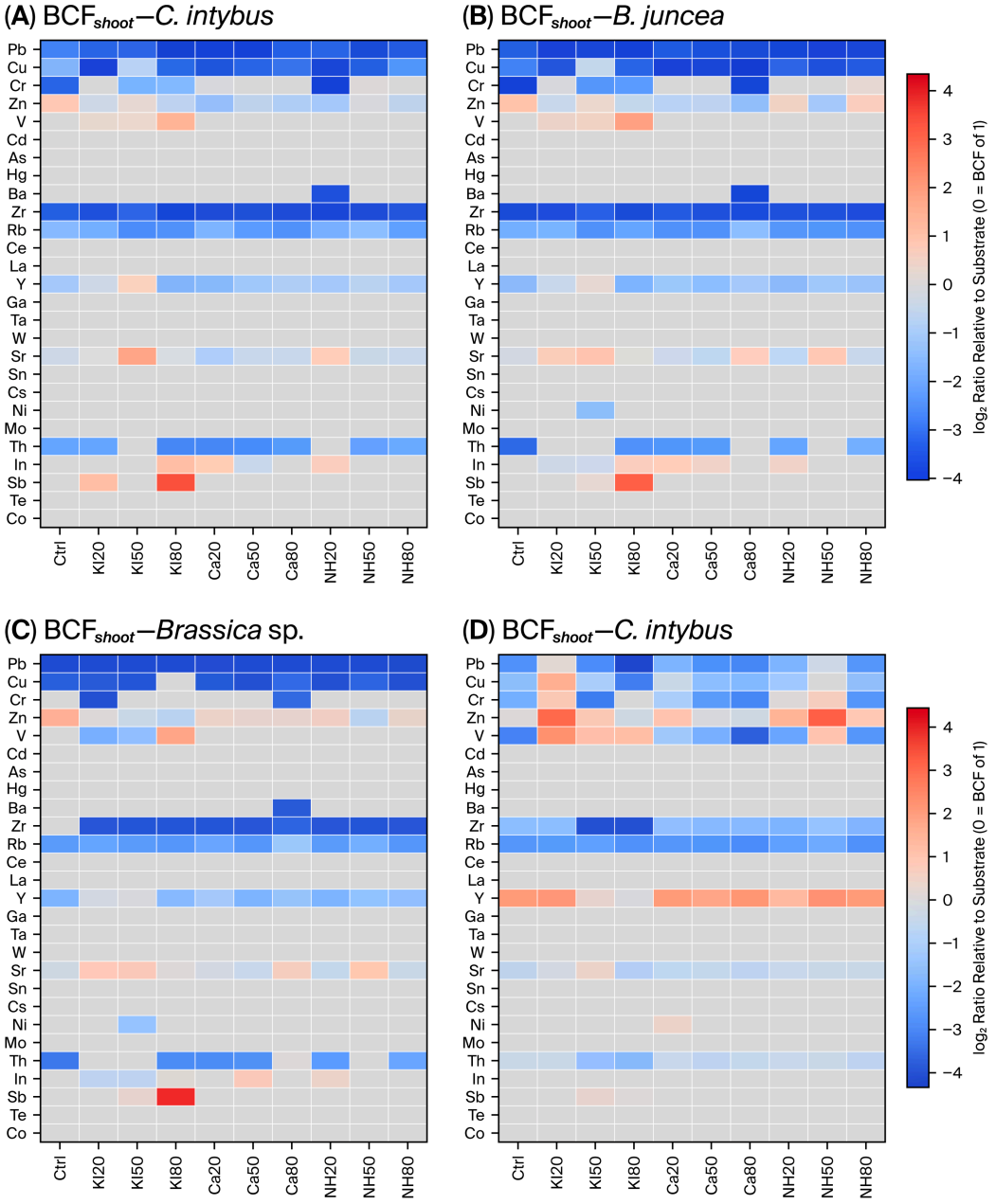

Figure 4. Root bioconcentration factors for the analysed elements in *Cichorium intybus* and *Brassica juncea*.

3.4. Treatment Responses Relative to Species-Specific Controls

Treatment responses relative to the corresponding species-specific controls were evaluated using absolute differences, fold changes, percentage changes and $\log_2$-transformed fold changes. The complete control-relative dataset is provided in Supplementary Table S3, while the overall patterns are visualised in Figure 5.

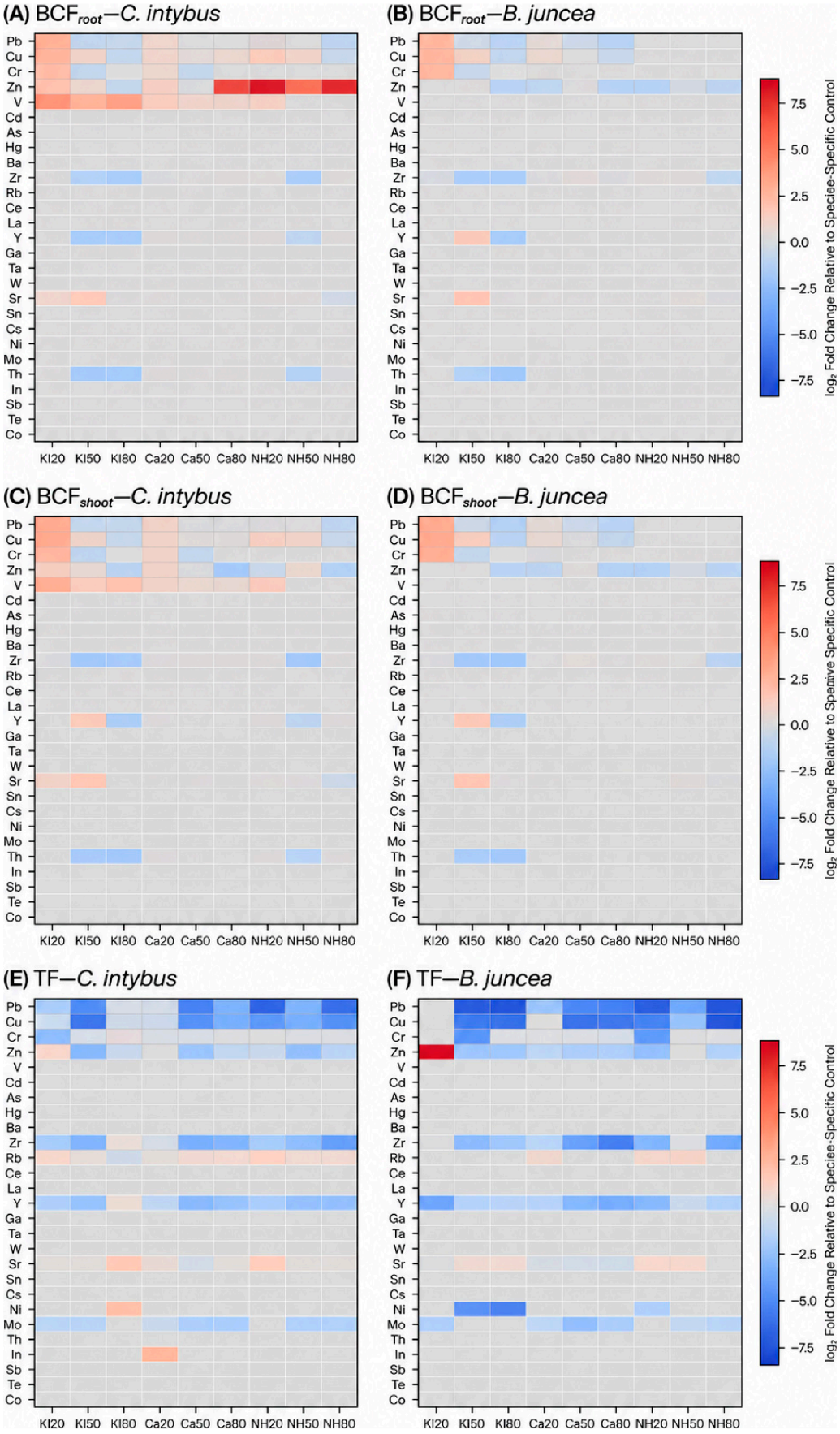

Figure 5. Heatmaps of $\log_2$-transformed fold changes in root bioconcentration, shoot bioconcentration and root-to-shoot translocation relative to the corresponding species-specific controls.

Exact control-relative metrics could be calculated for 385 treatment–element–index combinations, of these, 170 represented increases and 215 represented decreases relative to the corresponding species-specific controls. The coexistence of positive and negative responses confirms that the reagents did not produce a general enhancement of accumulation or translocation. The complete results for Δ, *FC*, percentage change and $\log_2 FC$ are presented in Supplementary Table S3 and visualised in Figure 5.

Among the 146 elements × species × reagent × index combinations for which exact values were available at all three doses, 88 showed non-monotonic responses., 33 demonstrated strictly decreasing patterns, only 25 showed successive increases from 20 to 80 mg kg^{-1}. Therefore, increasing reagent dose therefore did not generally result in a proportional increase in bioconcentration or translocation.

KI produced the clearest control-relative response for V in *C. intybus*. V BCF_{root} was 57.2, 22.0- and 24.3-fold higher than the control under KI20, KI50, and KI80, corresponding to values of 5.68, 2.18, and 2.41, respectively. Thus, all three doses enhanced root enrichment, but the strongest response occurred at the lowest dose.

The effects of KI on Cu and Zn in *C. intybus* were predominantly root-oriented. Under KI20, Cu BCF_{root} increased 12.9-fold, whereas BCF_{shoot} decreased to 0.77 of the control and *TF* decreased to 0.059 of the control. Similarly, Zn BCF_{root} increased 7.59-fold, while BCF_{shoot} decreased to 0.49 and *TF* to 0.064 of their respective control values. These responses indicate enhanced root accumulation without corresponding enhancement of shoot enrichment.

A comparable separation between root and shoot responses was observed for NH_4Cl. In *C. intybus*, NH_4Cl50 increased Zn BCF_{root} 9.13-fold and V BCF_{root} 20.0-fold relative to the control, however, Zn, BCF_{shoot} decreased to 0.56 of the control and *TF* decreased to 0.062. The treatment therefore produced a strong increase in root enrichment but not in transfer to above-ground tissues.

Zn in *Brassica juncea* exhibited the largest calculated fold changes in BCF_{root}. The control value was 0.0112, whereas the treatments produced values ranging from 0.903 to 6.868, corresponding to increases of 80.5- to 612.2-fold. These very high fold changes were amplified by the exceptionally low control denominator and should therefore be considered together with the absolute BCF values. In contrast, Zn BCF_{shoot} under the treatments was only 0.25–0.60 of the control value, while *TF* was substantially reduced in all variants.

Several treatments altered allocation rather than producing parallel changes in root and shoot enrichment. In *C. intybus*, KI50 reduced Y BCF_{root} to 0.29 of the control but increased BCF_{shoot} 2.96-fold and *TF* 10.1-fold, the same treatment reduced Zr BCF_{root} to 0.16 of the control while increasing BCF_{shoot} 1.76-fold and *TF* 11.25-fold. In *Brassica juncea*, NH_4Cl50 reduced Y BCF_{root} to 0.18 of the control and increased BCF_{shoot} 1.49-fold and *TF* 8.40-fold. These cases demonstrate that a large increase in *TF* may result partly from a reduction in root concentration and not solely from increased shoot accumulation.

Control-relative metrics were not calculated for censored comparisons. This restriction particularly affected Cd and elements for which either the control or treatment index was expressed as a lower or upper bound. Such treatments were retained in Supplementary Table S2 but were not included in the *FC*, percentage-change, $\log_2 FC$ or complete dose-series analyses.

3.5. Shoot Bioconcentration

Shoot bioconcentration was generally lower than root bioconcentration, although several element- and treatment-specific exceptions were observed (Figure 4; Table S2).

In *C. intybus*, all three quantified V leaf concentrations produced BCF_{shoot} values above 1 under KI treatment; the values increased from 1.25 at 20 mg kg^{-1} to 1.29 at 50 mg kg^{-1} and 2.39 at 80 mg kg^{-1}.

The highest Sr BCF_{shoot} in chicory was 3.20 under KI at 50 mg kg^{-1}. NH_4Cl at 20 mg kg^{-1} also produced shoot enrichment of Sr, with BCF_{shoot} = 1.71. The highest Y BCF_{shoot} was 1.80 under KI at 50 mg kg^{-1}.

For Zn, BCF_{shoot} exceeded 1 in the chicory control and under KI at 50 mg kg^{-1}, with values of 1.68 and 1.27, respectively. Most other Zn treatments showed substantial root accumulation but BCF_{shoot} values below 1.

In *Brassica juncea*, Zn BCF_{shoot} exceeded 1 in seven of the ten variants. T, with the highest value, 2.34, occurring occurring in the control. Among the reagent treatments, the highest Zn BCF_{shoot} was 1.42 under NH_4Cl at 20 mg kg^{-1}.

KI at 80 mg kg^{-1} produced the most pronounced V response in *Brassica* leaves, with BCF_{shoot} = 3.60. Sr shoot enrichment occurred under several treatments, including NH_4Cl at 50 mg kg^{-1}, where BCF_{shoot} reached 1.92, and KI at 20 and 50 mg kg^{-1}, where the values were both 1.57.

High BCF_{shoot} values were also calculated for Sb in individual samples. How-ever, the corresponding substrate and leaf concentrations were simultaneously quan-tified in only two variants per species. These isolated ratios were therefore not inter-preted as a consistent accumulation response.

3.6. Root-to-Shoot Translocation

The translocation patterns differed clearly among elements (Figure 6).

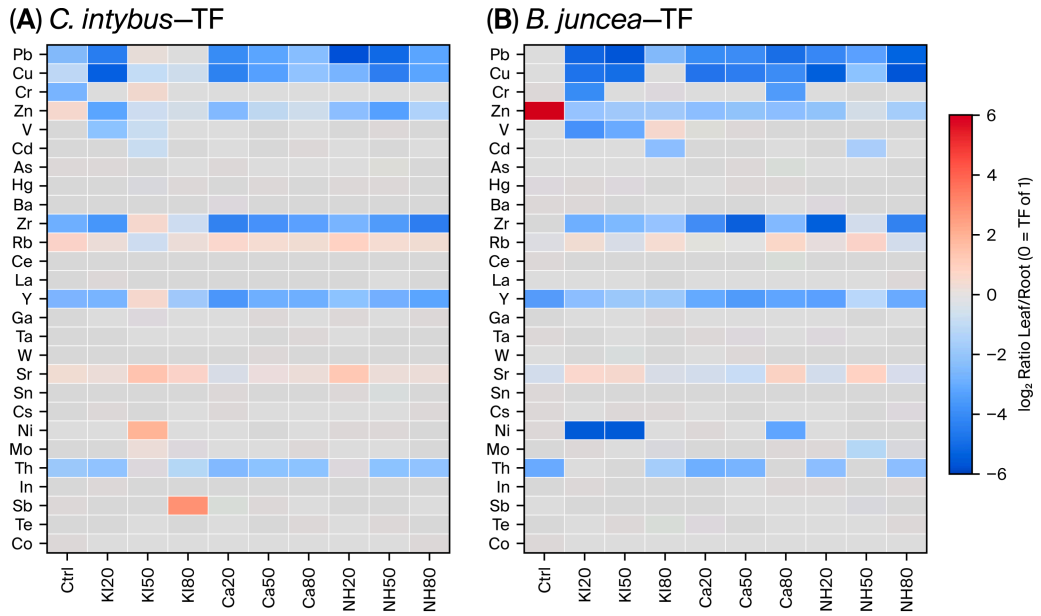

Figure 6. Root-to-shoot translocation factors for the analysed elements in *Cichorium intybus* and *Brassica juncea*.

Rb showed the most consistent transfer to above-ground tissues, with *TF* exceeded exceeding 1 in nine of the ten chicory treatments and six of the ten *Brassica* treatments. In *C. intybus*, the highest Rb *TF* values were 1.73 in the control and 1.71 under NH_4Cl at 20 mg kg^{-1}; in *Brassica juncea*, the maximum Rb *TF* was 1.71 under $CaCl_2$ at 80 mg kg^{-1}.

Sr was also readily transferred to chicory leaves, with *TF* values above 1 in nine of the ten treatments. The highest values were recorded under KI at 50 mg kg^{-1} and NH_4Cl at 20 mg kg^{-1}, reaching 2.45 and 2.26, respectively.

In *Brassica juncea*, Sr *TF* exceeded 1 in four treatments; the maximum value was 1.72 under NH_4Cl at 50 mg kg^{-1}, followed by 1.62 under $CaCl_2$ at 80 mg kg^{-1}.

The most distinct treatment-specific V translocation response occurred in *Brassica juncea* under KI at 80 mg kg^{-1}, where *TF* reached 1.62. Under the same treatment, V BCF_{shoot} reached 3.60, indicating that this response reflected both enrichment rela-tive to the substrate and transfer from roots to leaves.

Pb, Cu, Zr, Y, and Th were predominantly retained in the roots. Their *TF* values generally remained below 1 in both species, even when root bioconcentration was comparatively high. This pattern was particularly evident for Y, which showed con-sistently high BCF_{root} values but generally low *TF* values.

An exceptionally high Zn *TF* of 208.96 was obtained for the *Brassica* control. This ratio resulted from the combination of a very low root concentration of 1.15 mg kg^{-1} and a leaf concentration of 240.3 mg kg^{-1}. Because it represented an isolated value and differed by several orders of magnitude from the other Zn treatments, it was treated as an unstable treatment-specific ratio and was not interpreted as evidence of a general translocation pattern.

The reference value *TF* = 1 represents equal element concentrations in roots and leaves.

3.7. Treatment-Specific Response Patterns

None of the three reagents produced a uniform increase in bioconcentration or translocation across all elements, doses and plant species.

KI produced several of the strongest individual responses: at 20 mg kg^{-1}, it increased root bioconcentration of Pb, Cu, Cr, and V in *C. intybus* and of Cu and V in *Brassica juncea*; at 50 mg kg^{-1}, it was associated with high shoot bioconcentration and translocation of Sr and Y in chicory; and at 80 mg kg^{-1}, it produced the strongest shoot enrichment and translocation response for V in *Brassica juncea*.

NH_4Cl produced the highest Zn BCF_{root} in *C. intybus* at 50 mg kg^{-1} and the highest Cr BCF_{root} in *Brassica juncea* at 80 mg kg^{-1}. $CaCl_2$ produced the highest root bioconcentration of Zn and Y in *Brassica juncea*, particularly at 20 mg kg^{-1}.

The responses were not consistently dose-dependent: in many cases, the maximum coefficient occurred at 20 or 50 mg kg^{-1} rather than at the highest dose, and clear non-linear patterns were observed for Cu, Zn, Pb, Cr, and Y. Consequently, the results do not support a general assumption that raising the reagent dose systematically increases element uptake or translocation.

The observed responses demonstrate contrasting element-allocation strategies. Zn and Y showed substantial root enrichment, particularly in *Brassica juncea*, while Rb and Sr were more readily transferred to the leaves; meanwhile, Pb, Cu, Zr, Y, and Th were predominantly retained below ground. These findings identify potentially useful plant–reagent combinations but do not quantify total element removal because plant dry biomass was not measured.

4. Discussion

4.1. Species-Specific Patterns of Element Accumulation

The descriptive comparison of *Cichorium intybus* and *Brassica juncea* revealed clear species-specific differences in element uptake and internal allocation, although neither species showed consistently superior accumulation across all analysed elements. *Brassica juncea* more frequently exhibited higher root bioconcentration of Sr, Th, Y and Zn, whereas *C. intybus* generally showed higher BCF_{root} values for Rb. Differences were also evident in the above-ground tissues. Zn BCF_{shoot} exceeded 1 in seven *Brassica* treatments but in only two *C. intybus* treatments, while *C. intybus* more frequently showed greater

root-to-shoot transfer of Sr, Pb and Cu. These patterns indicate contrasting element-specific accumulation strategies rather than a universal advantage of either species. Because each species × treatment combination was represented by one composite analytical sample, the observed differences should be interpreted descriptively and not as statistically demonstrated species effects.

The stronger root accumulation observed for several elements in *Brassica juncea* is consistent with the ability of *Brassica* plants to absorb elements from the substrate and retain them in root tissues. *Brassica* species possess several physiological and biochemical mechanisms for limiting metal toxicity, including binding to phytochelatins, glutathione and metallothioneins, followed by sequestration in cell walls or vacuoles. Such mechanisms may produce high root concentrations without proportional transfer to above-ground organs [21,22]. Depending on the target element, these species may therefore contribute either to phytoextraction or to phyto-stabilisation.

Zn represented an important exception to a strictly root-dominant pattern in *Brassica juncea*. Although Zn frequently exhibited high BCF_{root} values, shoot enrichment also occurred in most treatments, consistent with previous evidence that Zn is more readily translocated than several non-essential elements in *Brassica* plants. Studies with *Brassica juncea* have reported *TF* values above 1 for Zn, whereas the transfer of Cd and Pb is commonly more restricted [22]. The comparatively effective transfer of Zn may be related to its essential role in plant metabolism and the presence of regulated transport pathways involved in nutrient acquisition and internal redistribution.

The results for *C. intybus* indicate a comparatively greater capacity to transfer selected elements from roots to leaves; this was particularly evident for Rb, for which BCF_{root} remained below 1 while *TF* exceeded 1 in most treatments. Higher *TF* values for Sr, Pb, and Cu were also observed in most direct comparisons with *Brassica juncea*. Previous studies similarly demonstrate that chicory can translocate selected elements to its above-ground biomass. Guérin et al. [23] observed root-to-leaf transfer of Cd and, to a lesser extent, Zn in chicory grown on contaminated soil, while also demonstrating that accumulation varied with cultivar and sampling time. Wu et al. [8] reported substantial Cd accumulation and translocation under controlled pot conditions, confirming that chicory can function as a potential Cd accumulator. These studies indicate that element allocation in *C. intybus* is dynamic and dependent on genotype, exposure conditions, and plant development.

However, field evidence shows that the accumulation capacity of *C. intybus* is strongly context-dependent: in naturally established vegetation on a reclaimed tailings pond in Bulgaria, chicory contained relatively low REE concentrations in its leaves, including 0.51 mg kg^{-1} Y, and its shoot bioconcentration factors remained below 1 [24]. The higher concentration ratios observed in the present controlled experiment should therefore be interpreted as evidence of potential uptake and internal allocation rather than as direct evidence of field-scale phytoextraction or phytomining performance.

The contrasting behaviour of Y and Rb further demonstrates why *BCF* and *TF* must be interpreted jointly. Y exhibited BCF_{root} values above 1 in nine of the ten treatments for each species, while *TF* generally remained below 1, indicating uptake from the substrate followed by preferential root retention. Rb showed the opposite pattern: root concentrations remained below those in the substrate, but the element was frequently transferred from roots to leaves. Therefore, a *TF* above 1 does not independently demonstrate effective phytoextraction; it indicates preferential allocation to shoots relative to roots but provides no information on whether the plant is enriched relative to the substrate.

The root-dominant accumulation of Y is consistent with findings for REEs in other non-specialised plant species. Gmur et al. [25] found that REE uptake and allocation varied among plant species and substrates, but BCF values remained below 1 and a sub-

stantial proportion of the accumulated elements were retained in the roots. Similarly, Richardson et al. [26] demonstrated that tissue type had a significant effect on REE concentrations, with roots generally accumulating more than shoots, while species and variety strongly influenced dry biomass production. These observations support the interpretation that high root concentrations may contribute to element retention or phytostabilisation but do not necessarily indicate suitability for shoot-based recovery.

Cd requires separate and cautious interpretation. It was below the analytical detection limit in all substrate samples; consequently, the corresponding BCF_{root} and BCF_{shoot} values represent lower bounds rather than exact coefficients. Cd was quantified in leaves, confirming uptake into above-ground tissues, but root concentrations were frequently below the detection limit. Exact *TF* values could therefore only be calculated when both root and leaf concentrations were quantitatively determined. The results support the occurrence of Cd uptake but do not permit a precise comparison of its accumulation efficiency between the two species or classification of either species as a Cd hyperaccumulator.

More generally, classification based solely on *BCF* or *TF* is inappropriate. Pot experiments restrict root development and may generate accumulation patterns that differ substantially from those under field conditions. Wu et al. [8] showed that chicory achieved considerably higher Cd concentrations in controlled experiments than in field trials and therefore described it as a potential Cd accumulator rather than assigning hyperaccumulator status solely from pot-derived coefficients. Likewise, recent REE phytomining studies emphasise that plant selection must consider not only concentration in tissues but also biomass production, tolerance, local adaptation, harvestability, and the feasibility of processing the enriched biomass [26,27].

Overall, the results indicate that species selection for assisted phytoremediation should be element- and objective-specific. *Brassica juncea* showed stronger potential for root accumulation and retention of several elements, including Y, Sr, and Th, whereas *C. intybus* more frequently promoted transfer to the leaves for elements such as Rb, Sr, Pb, and Cu. Root-dominant accumulation may be relevant to phytostabilisation, while transfer into harvestable shoots is required for phytoextraction and phytomining. However, because dry biomass was not measured, the present results describe concentration and allocation patterns but do not quantify total element removal or recovery yield.

4.2. Effects of KI, $CaCl_2$ and NH_4Cl Treatments

The effects of KI, $CaCl_2$, and NH_4Cl were element-, species-, and tissue-specific. None of the reagents produced a uniform increase in BCF_{root}, BCF_{shoot}, or *TF* across the analysed elements, and increasing the dose from 20 to 80 mg kg^{-1} did not generally result in a monotonic response. The treatments therefore acted as selective modifiers of element uptake and internal allocation rather than as universal enhancers of accumulation. Because each species × treatment combination was represented by one composite analytical sample, these patterns should be interpreted descriptively rather than as statistically demonstrated treatment effects.

All experimental variants, including the controls, received citric acid. Consequently, the control-relative responses represent the additional effects of KI, $CaCl_2$, or NH_4Cl superimposed on a common citric-acid amendment. Citric acid can promote element desorption and complexation in the rhizosphere and has previously enhanced Cr and Pb phytoextraction by *Brassica* plants while partially alleviating metal-induced physiological stress [17,18]. However, because the experiment did not include a control without citric acid, its independent contribution to element mobilisation cannot be determined.

Among the tested reagents, KI produced the clearest response for V. In *C. intybus*, V BCF_{root} increased from 0.099 in the control to 5.68, 2.18, and 2.41 under KI20, KI50, and

KI80, respectively. These values correspond to approximately 57-, 22-, and 24-fold increases relative to the species-specific control, with the strongest response occurring at the lowest dose. V BCF_{shoot} also increased from below 0.059 in the control to 1.25–2.39 under the three KI treatments. In *Brassica juncea*, the control V BCF_{root} was below 0.016, whereas values of 4.08, 3.37, and 2.23 were recorded under KI20, KI50, and KI80. Because the control was censored, an exact fold change could not be calculated. Under KI80, BCF_{shoot} reached 3.60 and *TF* reached 1.62, indicating that this treatment was associated with both tissue enrichment and effective transfer of V to the leaves.

The KI response was not equivalent for all elements. In *C. intybus*, Cu BCF_{root} increased from 0.271 in the control to 3.50 under KI20, representing an approximate 13-fold increase, but declined to 0.611 and 0.112 under KI50 and KI80, respectively. The corresponding BCF_{shoot} values remained below 0.35, indicating that the pronounced response under KI20 primarily reflected root retention. A similar pattern occurred for Zn: KI20 increased BCF_{root} from 1.18 to 8.95, while BCF_{shoot} decreased from 1.68 to 0.817 and *TF* from 1.42 to 0.091. Thus, KI markedly increased the relative Zn concentration in roots without improving transfer into harvestable above-ground tissues.

The choice of KI, and of the two chloride salts, was motivated by halide-assisted metal complexation: iodide and chloride form soluble complexes with several metals, a principle established for the induced accumulation of gold [14] and widely applied in hydrometallurgical chloride leaching, yet still little explored for the phytoextraction of other elements. Previous experiments have demonstrated that KI can induce the accumulation of selected target elements in both *Brassica juncea* and chicory, particularly in studies of Au phytomining [14]. These findings support the general capacity of iodide-containing treatments to alter element availability and plant uptake under specific conditions. For vanadium specifically, several non-exclusive mechanisms may be involved. Under the near-neutral, oxic conditions of the conditioned substrate, vanadium is expected to occur mainly as the pentavalent vanadate oxyanion ($H_2VO_4^-$/HVO_4^{2-}), a structural analogue of phosphate that can enter roots through phosphate-transport pathways. Iodide is a redox-active species capable of partially reducing V(V) to the more soluble vanadyl cation V(IV), while the accompanying K^+ may modify phosphate–vanadate competition at the root surface; any of these processes could enhance vanadate mobilisation and root uptake and would be consistent with the strong, low-dose V response observed under KI. However, the chemical behaviour established for Au cannot be applied directly to V, Cu, Zn or the other elements considered here. Substrate-solution concentrations, iodide complexes and element valence states were not measured; consequently, the results demonstrate KI-associated changes in accumulation but do not, on their own, identify the underlying mobilisation mechanism, which should be resolved in future work through speciation and rhizosphere-solution analysis.

$CaCl_2$ produced a predominantly root-oriented response, particularly for Zn in *Brassica juncea*: across the three doses, Zn BCF_{root} ranged from 5.51 to 6.87, whereas BCF_{shoot} ranged from 1.17 to 1.33 and *TF* remained between 0.173 and 0.213. The leaves were enriched relative to the substrate, but root concentrations remained substantially higher, indicating preferential below-ground retention. In *C. intybus*, $CaCl_2$20 increased Zn BCF_{root} from 1.18 to 2.39, whereas all three $CaCl_2$ treatments reduced BCF_{shoot} to 0.415–0.690 and *TF* to 0.173–0.722. Therefore, $CaCl_2$ did not improve shoot-based Zn extraction in chicory.

Several simultaneous processes may contribute to the $CaCl_2$ response. Chloride can form soluble complexes with selected elements and has been shown to increase Cd availability under particular soil conditions [16]. At the same time, Ca^{2+} may influence exchange equilibria, ionic strength, root–surface interactions, and competition among divalent ions; consequently, the response may vary among elements, plant species and

substrate conditions. The contrast between $CaCl_2$ and NH_4Cl is particularly informative because both reagents supplied chloride but differed in their accompanying cation, so their divergent effects cannot be attributed to chloride alone. The difference is most plausibly explained by the contrasting behaviour of the cations. Ammonium uptake by roots and, most importantly, the microbial nitrification of NH_4^+ to nitrate release H^+ and progressively acidify the rhizosphere; the resulting decrease in pH can enhance the desorption and solubility of several cationic metals, which is consistent with the strong, largely root-directed increases in Zn, V, Cr, Pb, and Cu bioconcentration recorded under NH_4Cl in *C. intybus*. Calcium, by contrast, is a divalent cation that competes with divalent trace metals such as Zn^{2+} for exchange and root-uptake sites and tends to raise ionic strength and promote colloid flocculation rather than to acidify the rhizosphere; this competitive, charge-screening behaviour is consistent with the predominantly root-retained Zn response and the limited shoot transfer recorded under $CaCl_2$. These interpretations remain hypotheses, because rhizosphere pH, solution composition, and element speciation were not measured; testing them would require monitoring of rhizosphere-solution chemistry in the proposed validation experiments. More broadly, although chloride-driven metal complexation is well established in hydrometallurgy, its influence on phytoextraction has rarely been examined; therefore, the contrasting $CaCl_2$ and NH_4Cl responses observed here also help to separate the role of the chloride ligand from that of its accompanying cation.

NH_4Cl produced some of the strongest root bioconcentration responses in *C. intybus*, particularly at the intermediate dose. Under NH_4Cl50, Zn BCF_{root} increased from 1.18 to 10.76, representing an approximately nine-fold increase relative to the control, and was accompanied by a decrease in BCF_{shoot} from 1.68 to 0.945 and in *TF* from 1.42 to 0.088. The same treatment increased V BCF_{root} from 0.099 to 1.99, corresponding to an approximately 20-fold increase, and also increased Cr, Pb, and Cu BCF_{root} from 0.226 to 1.65, 0.159 to 0.852, and 0.271 to 1.02, respectively. In most cases, however, the increase in root enrichment was not accompanied by a comparable increase in the leaves. NH_4Cl50 therefore promoted below-ground retention more clearly than shoot-based extraction in chicory.

The NH_4Cl response in *Brassica juncea* was more variable and also illustrates the need to interpret *TF* together with both *BCF* indices. Under NH_4Cl50, Y BCF_{root} decreased from 4.85 in the control to 0.859, while *TF* increased from 0.052 to 0.440; nevertheless, BCF_{shoot} remained below 0.4. The increase in *TF* therefore resulted largely from the lower root concentration rather than from strong enrichment of the leaves. A higher *TF* should not automatically be interpreted as evidence of improved phytoextraction when BCF_{shoot} remains low.

The absence of a consistent dose–response relationship was evident for all three reagents: the strongest Cu and Zn root responses to KI in *C. intybus* occurred under KI20 rather than at the higher doses, and the highest Zn BCF_{root} in chicory occurred under NH_4Cl50 rather than NH_4Cl80, while the Zn response to $CaCl_2$ in *Brassica juncea* remained relatively similar across the three doses. Element uptake depends on interactions among substrate pH, cation-exchange capacity, competing ions, element bioavailability, and plant physiology and therefore cannot be expected to increase proportionally with reagent dose [22,28]. The highest applied dose should consequently not be assumed to represent the most effective treatment.

Cd requires particularly cautious interpretation. It was below the analytical detection limit in all substrate samples, and the corresponding BCF_{root} and BCF_{shoot} values therefore represent lower bounds rather than exact coefficients. Exact *TF* values could only be calculated when Cd was quantitatively determined in both roots and leaves. Although the results confirm Cd uptake under several treatments, they do not support a precise ranking

of KI, $CaCl_2$, and NH_4Cl according to Cd mobilisation efficiency. Censored values were therefore excluded from the control-relative *FC* and log_2FC calculations.

Overall, no reagent can be identified as universally optimal. KI produced the most distinctive response for V and induced strong but frequently root-dominant accumulation of Cu and Zn; $CaCl_2$ promoted substantial Zn accumulation in *Brassica* roots but produced limited transfer to the leaves; and NH_4Cl generated marked element-specific increases in root bioconcentration in *C. intybus*, particularly at the intermediate dose, but these increases generally did not translate into greater shoot enrichment. Reagent selection must therefore be tailored to the target element, plant species, and intended remediation pathway. Root retention may be relevant to immobilisation-oriented applications, whereas harvest-based phytoextraction or phytomining requires enrichment of above-ground tissues together with sufficient harvestable biomass. Because dry biomass was not measured, the observed concentration responses cannot be translated into total element removal or recovery yields.

4.3. Implications for Assisted Phytoremediation as a Nature-Based Solution

The results demonstrate the potential of plant-based management of technogenic substrates, but they should not be interpreted as evidence of field-scale remediation effectiveness. The tested material originated from a historical mining waste-rock deposit rather than directly from an urban soil; nevertheless, it represents a relevant model for post-mining areas, industrial brownfields, and other disturbed sites where contamination, poor substrate quality and the need for vegetation establishment occur simultaneously. In such contexts, phytoremediation can provide a less disruptive alternative to excavation by maintaining soil cover and allowing treatment to proceed in situ. However, its suitability depends on site-specific contamination, land-use objectives, time constraints, and acceptable residual risk.

The contrasting responses of the two species have practical implications for designing assisted phytoremediation systems. *Brassica juncea* more frequently retained several elements in the roots, whereas *C. intybus* promoted greater transfer of selected elements into the leaves. These responses correspond to different remediation functions: root retention may contribute to immobilisation and reduced dispersal, while accumulation in harvestable shoots is required for actual removal from the site. Species selection should therefore be based on the target elements and remediation objective rather than on a general classification of a species as an accumulator. A mixed-species approach could potentially combine stable vegetation cover with complementary element-allocation strategies, although this possibility was not directly tested in the present experiment.

The distinction between phytoextraction and phytostabilisation is particularly important for the environmental value of the intervention. Root-dominant accumulation does not remove an element from the site unless the roots are excavated, which would disturb the substrate and partly negate the low-impact character of the approach. Therefore, root retention is more relevant where the objective is to reduce mobility and exposure rather than to decrease the total contaminant inventory. By contrast, elements transferred into leaves can be removed through periodic harvesting while maintaining much of the root system and vegetation cover, providing a closer fit with nature-based remediation, as long as harvested biomass is managed safely and contaminant return through leaf senescence, litter decomposition, or accidental consumption is prevented.

The use of mobilising agents introduces an additional trade-off: increasing element availability may improve uptake, but it may also increase the concentration of mobile elements in the soil solution and thereby enhance leaching or off-site transport. Chemically assisted phytoextraction can therefore be considered environmentally beneficial only when mobilisation is temporally synchronised with rapid plant uptake and does not create a

larger dissolved contaminant pool than the vegetation can capture. Similar concerns have been raised for conventional chelating agents, whose ability to increase uptake may be accompanied by groundwater contamination and persistent effects on soil chemistry [11,12].

The present results cannot be used to identify a reagent that could be applied universally: KI produced pronounced responses for selected elements, particularly V, whereas $CaCl_2$ and NH_4Cl frequently increased root accumulation without proportionally enhancing shoot enrichment. The absence of consistent dose-dependent responses further indicates that reagent application should be optimised for each combination of substrate, plant and target element. The lowest effective dose would generally be preferable because it would reduce reagent inputs and potential ecological side effects. Before field application, the treatments would require assessment of pore-water concentrations, leaching, changes in pH and salinity, nutrient availability, and responses of soil microorganisms and non-target vegetation.

The common application of citric acid to all experimental variants must also be considered when transferring the results to practice, as citric acid may increase element availability while also influencing plant tolerance and rhizosphere chemistry. Consequently, the present experiment evaluates the additional effects of KI, $CaCl_2$, and NH_4Cl against a citric-acid-treated control rather than against a completely untreated substrate. A field validation should therefore include both an untreated reference and a citric-acid-only treatment to distinguish the contribution of the organic acid from that of the inorganic reagents.

The simultaneous presence of potentially toxic elements and critical raw materials creates a possible link between remediation and resource recovery. Phytomining has been proposed for urban soils, mine wastes, and other low-grade secondary resources where conventional extraction is economically or environmentally unsuitable [29,30]. Plant-based recovery may therefore contribute to a circular approach in which contaminated land is managed while selected valuable elements are concentrated in biomass.

Nevertheless, the present Y results mainly indicate root retention and do not demonstrate conventional shoot-based phytomining. Commercial phytomining requires plants that combine high target-element concentrations in above-ground tissues with substantial biomass production, tolerance, repeated regrowth, and efficient harvesting. The suitability of a “metal crop” is also location-specific and depends on climate, substrate conditions and ecological compatibility [27]. The concentrations obtained in non-specialised plants should therefore be viewed as an initial screening signal rather than evidence that recoverable quantities of Y or other critical elements can already be produced.

Field evidence from reclaimed Bulgarian tailings similarly shows that naturally occurring vegetation can absorb REEs but shoot bioconcentration may remain low even after long-term ecosystem development [24]. This supports the use of locally adapted species for screening and revegetation, while also showing that natural establishment alone may not provide sufficient enrichment for resource recovery. Assisted systems may improve uptake, but the ecological costs of reagent application must be balanced against any increase in accumulation.

Even where plant accumulation is sufficient, phytomining does not end with harvesting; it includes a complete chain of phytoextraction, biomass enrichment, and final element recovery. Processing options may include drying, combustion, pyrolysis, hydrometallurgical extraction, or conversion of biomass into functional materials. These stages determine whether the accumulated elements become recoverable products or merely contaminated plant waste. Current research on REE and noble-metal phytomining identifies biomass processing and selective extraction as major technical and economic limitations [31].

Biomass management is also essential from a remediation perspective. Harvested plant material enriched with contaminants cannot be used as conventional fodder, compost

or unrestricted biomass, and inappropriate disposal could return accumulated elements to the environment or transfer them to another exposure pathway. Any field application must therefore include a predetermined route for collection, storage, transport, treatment, and final recovery or disposal. The environmental performance of the system should be evaluated across the full life cycle rather than only at the plant-uptake stage.

Several limitations prevent quantitative evaluation of the proposed approach. Dry biomass was not determined, so total element uptake and removal per plant, pot, or unit area cannot be calculated. Moreover, the use of one composite analytical sample per species × treatment combination prevents estimation of within-treatment variability and inferential assessment of reagent effects. The experiment also did not measure changes in the mobile substrate fraction, pore water, leachate, plant physiological stress, microbial communities, or contaminant concentrations before and after repeated harvest cycles. As a result, the current findings identify promising accumulation and allocation patterns but cannot establish remediation rates, required treatment duration, environmental safety, or economic viability. In addition, element valence states and speciation, rhizosphere-solution (filtrate) composition, and pH dynamics were not determined, so the mobilisation mechanisms underlying the observed reagent effects remain hypothetical and could not be confirmed. Because dry root and shoot biomass was not measured, absolute element uptake per plant or per unit area could not be quantified; therefore, the figures presented here are restricted to concentration-based indices rather than mass-based removal.

A subsequent validation should therefore use independent biological replicates and include untreated, citric-acid-only, and reagent-treated controls. It should also quantify dry root and shoot biomass, total element uptake, changes in substrate concentrations and geochemical fractions, pore-water and leachate chemistry, plant tolerance, and effects on soil biota. Repeated cultivation and harvesting would be required to determine whether accumulation is maintained and whether the substrate is progressively depleted. The final assessment should compare the environmental and economic performance of the full plant–reagent–harvest–biomass-processing system with alternative remediation options.

Overall, the study supports chemically assisted phytoremediation as a screening-stage nature-based approach rather than as an already validated remediation technology. Its principal contribution is the demonstration that plant species, target element, and reagent jointly determine whether accumulation is directed towards the roots or harvestable leaves, providing a basis for designing element-specific strategies for disturbed mining and industrial substrates. However, demonstrating an effective nature-based solution requires evidence that the intervention produces measurable contaminant reduction or safe immobilisation while maintaining vegetation, avoiding secondary pollution, and providing a feasible route for managing the contaminated biomass.

5. Conclusions

This study showed that element accumulation and allocation in plants grown on a technogenic mining substrate were controlled primarily by the interaction between plant species, target element, and mobilising treatment. Neither *Cichorium intybus* nor *Brassica juncea* was consistently superior across all analysed elements: *Brassica juncea* more frequently exhibited strong root accumulation of elements such as Y, Sr, Th, and Zn, whereas *C. intybus* generally promoted greater transfer of selected elements, including Rb, Sr, Pb, and Cu, towards the leaves. These contrasting patterns indicate that plant selection for assisted phytoremediation should be based on the target element and intended remediation pathway.

The effects of KI, $CaCl_2$, and NH_4Cl were similarly selective. The control-relative analysis showed both increases and decreases in BCF_{root}, BCF_{shoot}, and TF, while most

complete dose series were non-monotonic. KI produced the clearest response for V and also increased root accumulation of Cu and Zn under selected treatments. $CaCl_2$ promoted predominantly root-oriented Zn accumulation in *Brassica juncea*, whereas NH_4Cl generated marked increases in the root bioconcentration of several elements in *C. intybus*, particularly at the intermediate dose. These increases did not consistently result in greater shoot enrichment; therefore, no reagent can be identified as universally optimal, and the highest tested dose should not be assumed to provide the most effective response.

Joint interpretation of BCF_{root}, BCF_{shoot}, and *TF* was essential. High root bioconcentration accompanied by limited translocation indicates root-focused accumulation but does not, by itself, confirm phytostabilisation. Similarly, a *TF* above 1 may reflect preferential internal allocation without substantial enrichment relative to the substrate. Harvest-based phytoextraction requires enrichment of above-ground tissues, effective translocation, and sufficient biomass production. Because dry biomass was not measured, the present results describe concentration and allocation patterns but do not quantify total element removal or recovery yield.

The results support the further investigation of chemically assisted phytoremediation as a nature-based approach for post-mining areas, industrial brownfields, and other technogenic substrates. Its practical application would require independent biological replication, untreated and citric-acid-only controls, measurements of plant biomass and total uptake, repeated cultivation and harvesting cycles, and monitoring of pore water, leachate and mobile element fractions. Safe management and potential processing of the harvested biomass must also be incorporated into the remediation design. The findings therefore provide a screening-level basis for developing element-specific plant–reagent combinations, rather than evidence of an already validated field-scale remediation or phytomining system.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/pr14182910/s1, Table S1: Element concentrations in the substrate, root and leaf samples, including element-specific analytical detection information; Table S2: Root bioconcentration factors, shoot bioconcentration factors and root-to-shoot translocation factors for the analysed elements; Table S3: Absolute differences, fold changes, percentage changes and $\log_2$-transformed fold changes relative to the corresponding species-specific controls.

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Abbreviations

The following abbreviations are used in this manuscript:

Abbreviation	Definition
BCF	Bioconcentration factor
BCFroot	Root bioconcentration factor
BCFshoot	Shoot bioconcentration factor
$CaCl_2$	Calcium chloride
CRM(s)	Critical raw material(s)
FC	Fold change
KI	Potassium iodide
log_2FC	Base-2 logarithm of fold change
NBS	Nature-based solution(s)
NH_4Cl	Ammonium chloride
NPK	Nitrogen–phosphorus–potassium
n.c.	Not calculable
REE(s)	Rare earth element(s)
TF	Translocation factor
XRF	X-ray fluorescence

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