



Enhancing the Phytoextraction of Cd, Cu, Pb, and Zn by *Portulaca oleracea* in a Heavily Contaminated Soil Using Low Molecular Weight Organic Substances: Is Phytoremediation Viable?

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Abstract

Phytoremediation can be accelerated if contaminated soils are amended with releasing agents. We tested four such materials, citric acid (CA), EDTA, oxalic acid (OA), and tartaric acid (TA) at two doses, 20 and 40 mmol kg⁻¹, amended in a pot experiment to a heavily contaminated soil cultivated with purslane (*Portulaca oleracea*). We found that Cd extracted with DTPA remained unchanged in all treatments compared to the control except for the treatment of added EDTA at 40 mmol kg⁻¹ (“EDTA-40”). Similar was the case with Cu, Pb, and Zn. As a consequence, Cd in the aboveground plant material increased significantly from 1.21 (control) to 3.84 at EDTA-40 and 3.55 at EDTA-20 (mg kg⁻¹). Similar was the case with all other metals, with Pb exhibiting an impressive fivefold increase to 280.35 mg kg⁻¹ at EDTA-40 from the control. We conclude that EDTA was the most successful releasing agent among those tested, especially for Pb and Zn. However, we come to the conclusion that, based on calculations of the required time to meaningfully reduce soil metals contents, phytoremediation is not a practical option for extremely metal-elevated soils. These findings should be verified under field conditions.

Keywords Contaminated soils · Heavy metals · Organic amendments · Phytoremediation · Environmental phytomanagement

1 Introduction

Potentially toxic elements (PTEs) are collectively named those elements that may have toxic effects to plants if found at high contents in soil; among those, Cd, Cu, Pb, and Zn are very important, as half of them are also essential nutrients (Cu and Zn), while Cd and Pb do not have any known

physiological functions in plants (Zhao et al. 2023). Metals like those aforementioned are often found at elevated contents in soils affected by heavy industrial activities. One such case is Lavrio, an area in south Attica, Greece, renowned for its Ag and Pb, currently terminated, mining explorations since the 2nd millennium BC (Pappa et al. 2018). Such activities have led to extremities in PTE contents in soils

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around the wider area of Lavrio (Kalyvas et al. 2018), even in areas inside the town of Lavrio itself (Antoniadis et al. 2022). However high the total PTE contents may be, their availability is greatly dependent on a range of soil physicochemical properties. Although PTE mobility varies to a great extent depending on the nature and properties of soils, it is generally agreed that PTEs deposited over long periods of time (i.e., of centuries or even millennia) exhibit lower mobility compared to those deposited over short periods—a process related to the PTE ageing mechanisms in soil (Luo et al. 2023). Thus, in the case of Lavrio, although total PTE contents are extremely high, their mobility is rather mild or even low. In such case, a viable way of remediating PTE-contaminated soils may be to increase PTE mobility for their accelerated transfer from soil to plant through the process also known as phytoextraction (Lee et al. 2023). This can be achieved with the application to soil of organic substances of low-molecular weight; these low-molecular weight organic substances (LMWOSs) can be naturally occurring (most notable of which are citric, oxalic, and tartaric acids) or may be synthetic (of which, the most highly used is EDTA—ethylenediamine tetraacetic acid). In both cases, LMWOSs have the capability to bind metals to readily create polydentate (thus stable) chelates, which, if of sufficiently low-molecular weight, can be directly absorbed by plant roots, thereby increasing PTE availability (Shaheen and Rinklebe 2015; Zheng et al. 2022; Ahraz et al. 2022). The naturally occurring LMWOSs have two main sources in soil: (a) they are excreted from root tissues of non-stressed plants and tend to increase nutrient and PTE availability (Lu et al. 2021; Ghasemi-Fasaei et al. 2021); (b) they are the result of the decomposition of higher molecular weight organic substances due to microbial activity. The former typically occurs when plants absorb more cations than anions from the soil solution—the exudation of LMWOSs often function as the outcome of the balancing of charges of absorbed ions by plants. The latter is a process expected whenever there is an application of organic material to soil or when there is a flush of microbial activity, e.g., due to temperature increases. Whatever their derivation may be, natural LMWOSs are often found in higher concentration in plant rhizosphere than in non-rhizosphere (Yang et al. 2023). Also they are short-lived in soil, as they are readily decomposed further to simpler organic forms or they undergo a complete turnover into inorganic forms. The availability increase of PTEs depends on a series of factors such as the physicochemical nature of any given PTE, the physicochemical characteristics and contents of the organic substances, soil solution pH, plant species-specific responses, and other environmental conditions (Geng et al. 2020; Han et al. 2018; Singh et al. 2016; Wang and Mulligan 2013; Schwab et al. 2008).

Experimental data indicate that LMWOS-PTE complexes are highly soluble at high soil pH values (Walker et al.

2003). Hydroxylic and carboxylic groups of such organic substances can also be retained onto soil colloidal surfaces, clay minerals and organic matter, limiting the overall cation exchange capacity of soils, an effect that further contributes to the increased formation of organometallic complexes (Caporale and Violante 2016; Zhang et al. 2022). Thus, soil application of LMWOSs increases PTE mobility in the soil–plant interface and also their root-to-shoot translocation. The latter is possible due to the fact that PTE toxicity effects tend to be alleviated when PTEs are absorbed along with LMWOSs (Riyazuddin et al. 2022). Indeed, PTE complexes with LMWOSs exhibit lower toxicity to biomolecules found in the cytoplasm and the vacuoles compared to the toxicity induced by PTEs absorbed as free ions (Irtelli and Navari-Izzo 2006). For example, *Solanum nigrum* grown in an alkaline soil spiked with 50 mg Cd kg⁻¹ and added with 20 mmol kg⁻¹ of citric acid was found to increase biomass rather than decrease it (Gao et al. 2010). Similar results were reported for *Iris halophila* grown in a PTE-laden soil from mining activities treated with 10 mmol kg⁻¹ of citric acid, which was found to have a 43% increase in aerial biomass compared to the control (Han et al. 2018). Sun et al. (2021) reported that the effectiveness of the LMWOSs differed greatly among them, with citric acid being the most effective, and oxalic or tartaric acids the least. As for EDTA, it often exhibits higher ability to increase PTE mobility over other LMWOSs (Sabir et al. 2014; Wu et al. 2003). However, the EDTA low-degradation rates in soil, combined with the limited EDTA sorption by soil colloids, may lead to environmental concerns due to increased risk of its extended leaching and plant uptake of PTEs (Ali et al. 2019; Nascimento et al. 2021). In addition, EDTA may lead to phytotoxic symptoms and negative effects on mycorrhizal and soil fungi populations (Grčman et al. 2001; Beltyukova et al. 2023). This is why there have been attempts to test degradable synthetic chelates, like iminodisuccinic acid (ISA) and glutamate–N, N–diacetic acid (GLDA) (Wang et al. 2020). Indeed, natural biostimulants and LMWOSs are rapidly decomposed in soils; therefore, their organometallic complexes are considerably more short-lived compared to EDTA (Ali et al. 2019; Wu et al. 2003; Grammenou et al. 2023). Although there is a lot of research concerning the fate of LMWOSs in forming complexes with PTEs, most of the reported work concerns research efforts where both PTEs and LMWOSs are spiked in the soils (e.g., Jalali et al. 2023). Thus, there is still much to be explored in regard to their effect in soils with extremely high non-spiked PTE contents, especially Cd, Cu, Pb, and Zn. The role of such organometallic complexes may be of high importance if used in phytoremediation programs for soils heavily contaminated with PTEs (Amin et al. 2018; Shaheen et al. 2023). Due to the fact that most of the research works deal with the effects of LMWOSs in soils where PTE have been spiked prior to

the experimentation, there is still much to be elucidated for “real life” cases concerning soils already contaminated with PTEs, especially when dramatically enriched. In such cases, the effect of LMWOSs in altering PTE dynamics is not clear and needs to be evaluated.

Purslane (*Portulaca oleracea*) may be used both for human consumption and for non-food purposes (i.e., medicinal uses; Petropoulos et al. 2016; Subpiramanyam 2021). Purslane growth in soils with elevated PTE contents has been tested in the past (Wei et al. 2005; Levizou et al. 2016; Javed et al. 2017; Elshamy et al. 2019). However, this species has never been tested in relation to PTE bioavailability in non-spiked soils where PTEs have been deposited over long periods of millennia and where PTE uptake is tested when LMWOSs are added with the aim of boosting their uptake. The aim of this work was to (a) study the bioavailability of Cd, Cu, Pb, and Zn in the soil–plant interface of a heavily contaminated soil; (b) assess the effectiveness of four LMWOSs as mobilizing agents (three of which naturally occurring—citric acid, oxalic acid, tartaric acid, and one synthetic—EDTA) for increasing the uptake of PTEs; and (c) evaluate purslane as a potential species to be used for the phytoremediation of this soil heavily contaminated with Cd, Cu, Pb, and Zn. By this study, there may be significant benefits concerning the exploration of phytomanagement programs of heavily contaminated soils with inorganic contaminants by a variety of soil end-users, such as soil practitioners, soil scientists, and policy makers.

2 Materials and Methods

2.1 Experimental Design, Plant Growth and Measurements

A pot experiment was established using a soil sampled from an olive field in the town of Lavrio (37.719311° N, 24.044154° E). The exact settings of sampling can be found in Antoniadis et al. (2022). The area is renowned for its historical (now discontinued) mining activities known to have commenced in ca. the 2nd millennium BC (Panagopoulos et al. 2009). These activities have resulted in extremely high pseudo-total contents in soil concerning Cd (measured in that specific spot as equal to 101.9), Pb (26,526.4), and Zn (17,652.6), while Cu was mildly elevated (181.6) (all values in mg kg⁻¹). The soil was calcareous (CaCO₃ 7.9%), hence alkaline (pH 8.0; 1:2.5 H₂O), and also light-textured (sand 79.6%, silt 11.6%, clay 8.8%—a loamy sand), with low organic C content (1.1%), and electrical conductivity of 192 μS cm⁻¹ (analyses as per Rowell 1994). This heavily contaminated soil was transferred to the Laboratory of Soil Science in the University of Thessaly, where it was allowed to be air-dried. After this, it was passed through a sieve with

openings of 5 mm, and 1000-g portions of it were placed into 2-L pots. A total of 90 pots were filled with this quantity of soil. The pots were then watered, and soil moisture in pots was kept constant with frequent water additions to 2/3 of the soil's water holding capacity. Seeds of purslane (*Portulaca oleracea*) were planted in seedling trays filled with that same soil and watered regularly. After 25 days of planting, the vigorous seedlings were transplanted to the pots—one seedling per pot. The transplanting date was considered the first day of the experiment (21st of October 2020). The pots were placed in a greenhouse where they were protected from the elements, although light and temperature were not controlled. During the plant growth, pots' positions were exchanged regularly to compensate for any differences in light and temperature. On Day 10 (the 30th of October 2020) of the experiment, NPK were applied at an equivalent rate of 200 kg N ha⁻¹, 188 kg of P₂O₅ ha⁻¹ and 212 kg of K₂O ha⁻¹ (accounting for effective rhizosphere depth of 15 cm and soil bulk density 1.33 g cm⁻³). On Day 40, an additional amendment equivalent to 100 kg N ha⁻¹ was also dispensed to all treatments. On Day 45 of the experiment (5th of December 2020), commercially obtained low-molecular weight organic substances (LMWOSs; citric, oxalic and tartaric acids, and the synthetic chelate EDTA), were applied to the pots at two concentrations equal to 20 and 40 mmol kg⁻¹ soil. For the application, solutions of 200 mmol L⁻¹ of the four LMWOSs were prepared by solubilizing in four different flasks 38.42 g of citric acid (CA; C₆H₈O₇), 18.01 g of oxalic acid (OA; C₂H₂O₄), 30.02 g of tartaric acid (TA; C₄H₆O₆), and 67.24 g of EDTA-Na₂ (EDTA; C₁₀H₁₄N₂O₈·2Na·2H₂O) per L of H₂O. For the treatment of 20 mmol kg⁻¹, 100 mL of these 200-mM solutions were applied per pot, while 200 mL were applied for the 40 mmol kg⁻¹. Thus, the treatments are thereafter referred to as CA-20 (for citric acid added at 20 mmol kg⁻¹), CA-40 (citric acid added at 40 mmol kg⁻¹), and, similarly, OA-20 and OA-40 for oxalic acid at 20 and 40 mmol kg⁻¹, TA-20 and TA-40 for tartaric acid at 20 and 40 mmol kg⁻¹, and EDTA-20 and EDTA-40 at 20 and 40 mmol kg⁻¹. Each treatment of the four agents at the two concentrations resulted in nine different treatments (i.e., control plus 4 agents × 2 concentrations) and was replicated 10 times, hence resulting in 90 pots. These PTE-mobilizing agents were applied relatively late in the growth experiment due to the fact that the naturally occurring LMWOSs are typically short-lived, so that their effect would be more evident to the plants (Meers et al. 2005). The added agents are highly soluble and thus homogenous distribution within the pots was not considered to be a problem.

The experiment ran until the 21st of December 2020, i.e., it lasted for 61 days. On the harvest day, plant height was recorded just before aerial plant tissues were cut with non-metallic scissors at the soil level and rinsed with distilled water. The aerial biomass was then harvested and placed in

pre-weighed paper bags. Immediately after the aerial plant harvest, soil was also sampled taking three cores from top to bottom in each pot and then the three subsamples per pot were mixed together into one composite sample. Soil samples were placed into paper bags, taken to be air-dried (for 3–4 days), and then sieved through a 2-mm sieve. On the same day after the soil sampling, plant roots were also recovered by delicately rinsing all adhered soil particles from root hairs and placed into pre-weighed paper bags. All plant biomass (aerial and roots) were placed in a forced-draught oven at 70 °C for 2 days, after which the dry biomass was recorded.

Subsequently, Cd, Cu, Pb, and Zn were extracted and analyzed both in plant biomass and soil as follows: For the biomass (roots and aerial biomass), 1.0 g of pulverized plant tissue was dry-ashed at 500 °C for 4 h and extracted with 10 mL of 20% HCl (Jones and Case 1990). For the soil samples, there was a 2-h extraction with DTPA-CaCl₂ in a 1:2 soil:solution suspension which was then centrifuged at 2000 rpm and filtered through a slow filter paper (Lindsay and Norvell 1978). In all plant and soil extracts, the four metals were measured with atomic absorption spectrophotometry (Perkin Elmer A330).

2.2 Secondary Indices

Based on the primary data, some indices were calculated as follows: (a) soil-to-plant transfer (transfer coefficient, TC), equal to metal content in plant aerial biomass over the metal pseudo-total content in soil (Antoniadis et al. 2017); (b) root-to-shoot translocation (translocation factor, TF), equal to metal content in aerial biomass over metal content in roots. For these two indices, values approaching, or exceeding, 1.0 are indications of the plant species being suitable to be used for phytoextraction (Yan et al. 2020). Moreover, we calculated metal uptake as follows: Uptake by the plant (units, mg of PTE in aerial biomass per pot or per kg soil), equal to the multiplication of PTE contents in biomass (in mg PTE kg⁻¹ plant) with biomass yield (in g of plant per pot or per kg soil) divided by 10³ for unit conversion from g to kg. Also, based on Uptake, the number of harvests of the aerial biomass in order to halve the pseudo-total soil content of PTEs ($H_{1/2}$) was calculated, as follows: $H_{1/2} = 0.5 \times (\text{pseudo-total soil PTE content, mg of PTE in soil per kg soil}) / \text{Uptake per harvest (mg of PTE in plant per kg soil per harvest)}$.

2.3 Statistical Analysis and Data Quality Control

Data quality control was performed by systematically using blanks and soil and plant reference materials in each extraction batch. The percentage of recovery of the four extracted metals from the soil and plant reference materials ranged

between 92 and 108%. All analyses were performed in triplicates and acceptable coefficient of variation was less than 15%. The primary data underwent a one-way ANOVA (analysis of variance). Such analysis was preferred because (a) of its simplicity, and (b) it provides sufficient in-depth information so that significant differences may be easily identified. The level of significance of 95% ($p < 0.05$) was selected after testing for the normal distribution and homogeneity of variances; also data underwent a Post-hoc analysis according to Duncan. In this analysis, the factor was the treatments of added LMWOSs and dependent variables of the soil and plant analyzed parameters.

3 Results

3.1 Purslane Growth Characteristics and its Cd, Cu, Pb, and Zn Contents in Aerial Parts and Roots

Plant growth parameters measured were height, and dry weights of the aerial biomass and roots of purslane (Table 1). As for the height, the various treatments did not affect it, as average values across amendments were found with non-significant differences, ranging from 20.25 cm (control) to 23.47 cm (at EDTA-40). Similar was the case with the aerial dry weight, where differences were marginal and non-significant (minimum was 0.472 g at control and maximum 0.656 g at EDTA-20). Root dry weight was similarly found to have no significant differences among treatments; they ranged from 0.124 g (control) to 0.174 g (OA-20).

Cadmium content in purslane roots was 10.72 mg kg⁻¹ at control, and increased to 14.34 mg kg⁻¹ at CA-20, although the difference was not significant. At OA-20 Cd content was decreased to 6.19 mg kg⁻¹, significantly different from the control (Fig. 1). Copper in roots increased significantly from

Table 1 Growth parameters of purslane (height in cm, stems, leaves, and roots mg of dry weight (DW) per pot) in the treatments of the four mobilizing agents (citric acid, EDTA, oxalic acid, and tartaric acid) added in soil at 20 and 40 mmol kg⁻¹

Treatments	Height cm	Aerial g pot ⁻¹	Roots g pot ⁻¹
Control	20.25	0.472	0.124
Citric acid 20 mmol kg ⁻¹	22.40	0.544	0.160
Citric acid 40 mmol kg ⁻¹	22.46	0.508	0.136
EDTA-20 mmol kg ⁻¹	23.47	0.656	0.160
EDTA-40 mmol kg ⁻¹	22.37	0.584	0.164
Oxalic acid 20 mmol kg ⁻¹	21.81	0.516	0.174
Oxalic acid 40 mmol kg ⁻¹	21.08	0.552	0.146
Tartaric acid 20 mmol kg ⁻¹	21.70	0.584	0.158
Tartaric acid 40 mmol kg ⁻¹	21.95	0.584	0.148
Sign	NS	NS	NS

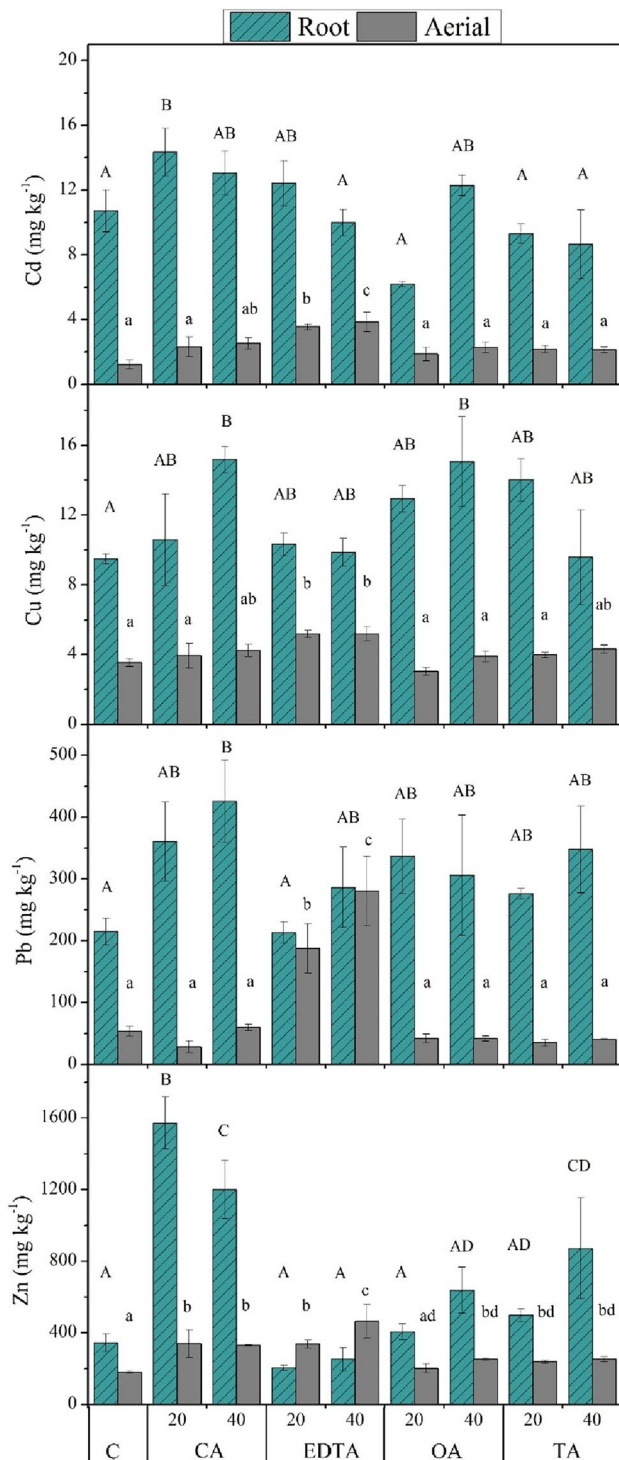


Fig. 1 Contents of Cd, Cu, Pb, and Zn in the root and aerial part of purslane in the treatments of the four mobilizing agents (C, unamended control; CA, citric acid; ED, EDTA; OA, oxalic acid; TA, tartaric acid) added in soil at 20 and 40 mmol kg⁻¹

9.49 mg kg⁻¹ (the lowest, at control) to 15.18 mg kg⁻¹ at CA-40, while all other treatments exhibited non-significant differences. Lead at control (215.03 mg kg⁻¹) was the lowest

and increased significantly to 425.87 mg kg⁻¹ at CA-40, with all other treatments being non-significant compared to the control. In the case of Zn, its content at control was 344.34 mg kg⁻¹, and had a significant 4.5-fold increase at CA-20 (1572.96 mg kg⁻¹); Zn at control also differed significantly from that at CA-40 (1200.62 mg kg⁻¹) and TA-40 (872.82 mg kg⁻¹).

As for the content of Cd in the aerial parts of purslane, it was 1.21 at control, and it exhibited a significant increase at CA-40 (2.52), while it was 2.55 at EDTA-20, and 3.84 at EDTA-40 (all values in mg kg⁻¹), with all other treatments having non-significant differences from the control (Fig. 1). Copper at control was 3.52, a value that exhibited significant differences only 2 to Cu at EDTA-20 (5.18) and EDTA-40 (5.19), with the two EDTA treatments having no differences between them (values in mg kg⁻¹). Similar was the case for Pb, where the value at EDTA-40 (280.35) was fivefold higher than that at control (53.73), while that at EDTA-20 (187.66) was significantly different from both EDTA-40 and the control (values in mg kg⁻¹). As for Zn, EDTA-40 was, similar to all other metals, the highest among the treatments with a value of 464.04, significantly higher from all other treatments; compared to the control (180.17), the treatments with significantly higher Zn content were CA-20, CA-40, and EDTA-20 (with values of 338.71, 329.47, 336.82, respectively) (all values in mg kg⁻¹).

3.2 Soil Extractions of Cd, Cu, Pb, and Zn with DTPA

Soil extraction of available Cd with DTPA was 7.06 at control and exhibited a significant increase at EDTA-40 to 9.74 (values in mg kg⁻¹; Fig. 2). No other treatment was significantly different from the control. As for Cu, EDTA-40 was the highest (3.61) and differed significantly from all other treatments, while the control (2.05, both values in mg kg⁻¹), which was the lowest, also differed from all other treatments. Lead extraction at control equalled 607.35; the only two treatments with significant differences were those of EDTA-20 (997.55) and EDTA-40 (1356.75); the two EDTA treatments were also different between each other (values in mg kg⁻¹). Similar to the previous metals, DTPA-extractable Zn had its highest value at EDTA-40 (662.00) and was significantly different from all other treatments. Zinc at control (254.130) was the lowest (units in mg kg⁻¹).

3.3 Soil and Plant Indices

The index of the soil-to-plant transfer of Cd (TC) was the highest at EDTA-40 (37.7×10^{-3} ; unitless), significantly different from the control (11.9×10^{-3} —the lowest among the Cd TC values), and all other treatments except for EDTA-20 (Table 2). As for Cu, its TC at EDTA-20 and EDTA-40 were almost identical (28.5×10^{-3} and

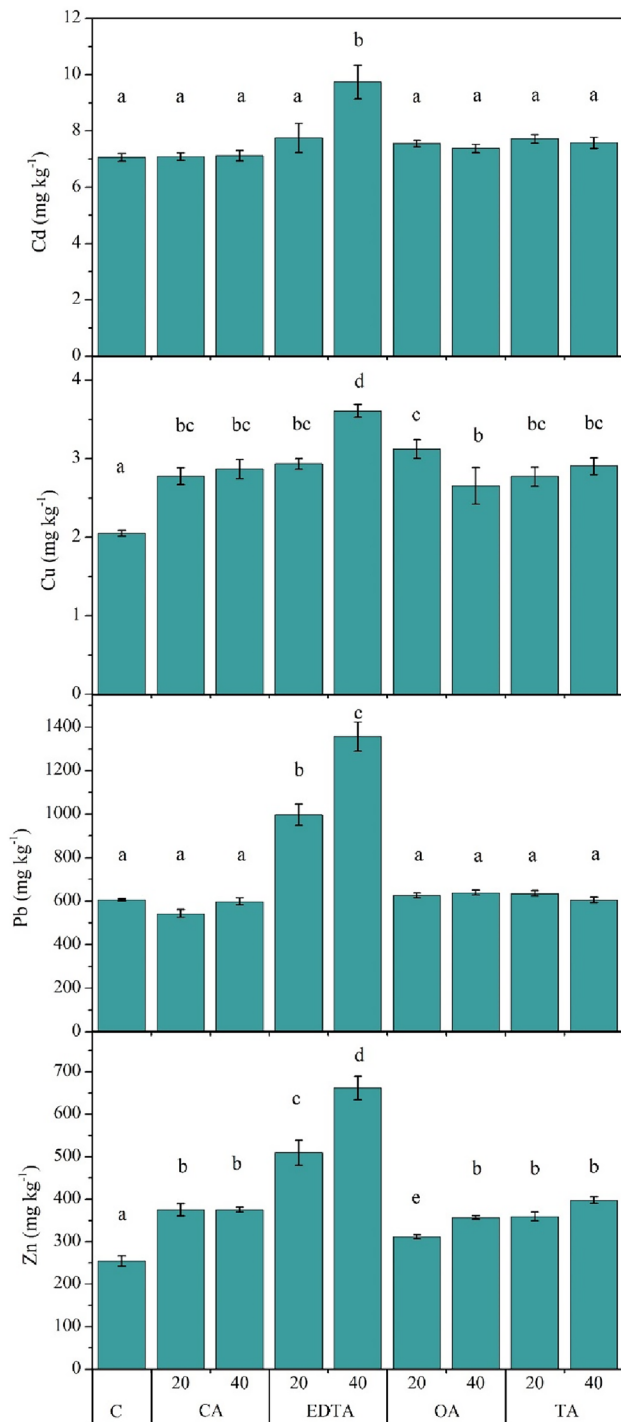


Fig. 2 Contents of Cd, Cu, Pb, and Zn in the soil extractions With DTPA in the treatments of the four mobilizing agents (C, unamended control; CA, citric acid; ED, EDTA; OA, oxalic acid; TA, tartaric acid) added in soil at 20 and 40 mmol kg⁻¹

28.6×10^{-3} , respectively), and significantly higher from all other treatments, except for CA-40 and TA-40. Lead TC did not differ among any of the treatments, except for EDTA-20 (7.1×10^{-3}) and EDTA-40 (10.6×10^{-3}) which

were significantly higher than the rest of the treatments. Zinc TC had a similar trend as the aforementioned metals, with EDTA-40 exhibiting the highest value (26.3×10^{-3}) and that of control (10.2×10^{-3}) being low and non-significant compared to most of the other treatments (more precisely, OA-20, OA-40, TA-20, and TA-40). When comparisons were made among metals across same treatments, Cd was found to be the metal with the highest TC value in 8 out of the 9 treatments and Pb the metal with the lowest TC in all treatments.

The TF for Cd revealed that the highest value was recorded at EDTA-40 (0.386), significantly higher from the control (0.130—the lowest), CA-20, and OA-40 (Table 2). Concerning the Cu TF, three treatments exhibited the highest values, EDTA-40 (0.539), TA-40 (0.518), EDTA-20 (0.504), while that of the control (0.362) did not have significant difference from these values. The Pb TF surpassed the threshold of unity at EDTA-40 (1.014), a value which was non-significantly different to that of EDTA-20 (0.878), but was significantly different from all other treatments. As for the Zn TF, the threshold of TF = 1.0 was surpassed in both EDTA treatments, with EDTA-40 having a TF = 2.017 and EDTA-20 a TF = 1.670; both values being significantly higher than all other treatments. When the four metals were compared across same treatments, it was revealed that Zn had the highest TF value compared to Cd, Cu, and Pb in almost all treatments, except for CA-20, CA-40, OA-40, and TA-40, where the differences among metals were non-significant.

Uptake of the four studied elements, an index combining metal contents and aerial plant biomass yield, showed that EDTA-20 (2.69) and EDTA-40 (2.41) had the highest uptake (units, μg of Cd in plant per pot or per kg soil), while all other treatments were lower and non-significant among them (Table 3). Likewise, Cu uptake was significantly higher at the two EDTA treatments compared to the other treatments (EDTA-20 = 3.93; EDTA-40 = 3.26 $\mu\text{g pot}^{-1}$). Lead uptake was 174.92 $\mu\text{g pot}^{-1}$ at EDTA-40 and 141.79 $\mu\text{g pot}^{-1}$ at EDTA-20, both of which were significantly higher than all other treatments. Similar trends were also recorded for Zn uptake: that at EDTA-40 was the highest (299.68), significantly different from the control (the lowest—93.70), CA-40, OA-20, OA-40, TA-20, and TA-40 (units; $\mu\text{g pot}^{-1}$). Based on the metal uptake data, we calculated the number of harvests needed to halve the pseudo-total metal contents ($H_{1/2}$; Table 3). In all four metals, EDTA lowered $H_{1/2}$ compared to the control: In Cd, however, all amendments were significantly lower from the control but without further differences among them. For Cu, $H_{1/2}$ was 23×10^3 at EDTA-20 (the lowest), a significant ca. twofold decrease from the

Table 2 Soil-to-aerial plant transfer coefficient (TC; metal concentration in aerial over total metal concentration in soil) (multiplied by a factor of 10^3 for clarity) and root-to-shoot translocation factor (TF; metal concentration in aerial parts over metal concentration in roots)

	TC $\times 10^3$					TF				
	Cd	Cu	Pb	Zn	Sign	Cd	Cu	Pb	Zn	Sign
Control	11.9 ^{aB}	19.4 ^{abC}	2.0 ^{aA}	10.2 ^{aB}	***	0.130 ^{aA}	0.362 ^{abBC}	0.294 ^{aAB}	0.549 ^{aC}	*
Citric acid 20 mmol kg ⁻¹	22.9	21.7 ^{abB}	1.1 ^{aA}	19.2 ^{cB}	*	0.175 ^{aAB}	0.430 ^{abB}	0.092 ^{aA}	0.223 ^{aAB}	NS
Citric acid 40 mmol kg ⁻¹	24.8 ^{bcB}	23.3 ^{bcB}	2.2 ^{aA}	18.7 ^{bcB}	***	0.202 ^{abAB}	0.280 ^{aB}	0.151 ^{aA}	0.284 ^{aB}	NS
EDTA-20 mmol kg ⁻¹	34.9 ^{cdD}	28.5 ^{cC}	7.1 ^{bA}	19.1 ^{cB}	***	0.294 ^{abA}	0.504 ^{abB}	0.878 ^{bB}	1.670 ^{bcC}	**
EDTA-40 mmol kg ⁻¹	37.7 ^{dB}	28.6 ^{cB}	10.6 ^{cA}	26.3 ^{dB}	*	0.386 ^{bA}	0.539 ^{bA}	1.014 ^{bA}	2.017 ^{bB}	*
Oxalic acid 20 mmol kg ⁻¹	18.4 ^{abB}	16.7 ^{aB}	1.6 ^{aA}	11.4 ^{abB}	**	0.300 ^{abB}	0.234 ^{aB}	0.125 ^{aA}	0.494 ^{aC}	***
Oxalic acid 40 mmol kg ⁻¹	22.2 ^{abC}	21.5 ^C	1.6 ^{aA}	14.3 ^{abcB}	***	0.183 ^{aA}	0.267 ^{aAB}	0.186 ^{aA}	0.425 ^{aB}	NS
Tartaric acid 20 mmol kg ⁻¹	21.4 ^{abC}	21.9 ^{abC}	1.3 ^{aA}	13.5 ^{abcB}	***	0.239 ^{abB}	0.288 ^{aB}	0.128 ^{aA}	0.481 ^{aC}	***
Tartaric 40 mmol kg ⁻¹	20.8 ^{abC}	23.8 ^{bcC}	1.5 ^{aA}	14.3 ^{abcB}	***	0.303 ^{abA}	0.518 ^{bA}	0.125 ^{aA}	0.388 ^{aA}	NS
Sign	**	**	***	**		NS	*	***	***	

Different small letters within each column indicates significant differences among treatments at $p < 0.05$

Different capital letters within each raw indicates significant differences among treatments at $p < 0.05$

NS Non-significant

*Significant at $p < 0.05$

**Significant at $p < 0.01$

***Significant at $p < 0.001$

Table 3 Uptake (in μg of metal absorbed by plant per pot), and the number of harvests (in 10^3) necessary to halve total soil concentrations ($H_{1/2}$) of the four studied metals (Cd, Cu, Pb, and Zn) to purslane in the treatments of the 4 mobilizing agents (citric acid, EDTA, oxalic acid, and tartaric acid) added in soil at 20 and 40 mmol kg⁻¹

Treatment	Uptake				$H_{1/2} \times 10^3$			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
Control	0.68 ^a	1.84 ^a	28.40 ^a	93.70 ^a	102 ^b	54 ^{bc}	553 ^{ab}	102 ^c
Citric acid 20 mmol kg ⁻¹	1.34 ^a	2.34 ^{ab}	16.25 ^a	197.40 ^{abc}	44 ^a	42 ^{abc}	1179 ^b	51 ^{ab}
Citric acid 40 mmol kg ⁻¹	1.01 ^a	1.73 ^a	24.73 ^a	136.21 ^{ab}	51 ^a	54 ^{bc}	563 ^{ab}	67 ^{abc}
EDTA-20 mmol kg ⁻¹	2.69 ^b	3.93 ^c	141.79 ^b	257.51 ^{bc}	19 ^a	23 ^a	105 ^a	35 ^a
EDTA-40 mmol kg ⁻¹	2.41 ^b	3.26 ^{bc}	174.92 ^b	299.68 ^c	23 ^a	30 ^{ab}	85 ^a	35 ^a
Oxalic acid 20 mmol kg ⁻¹	1.12 ^a	1.75 ^a	24.61 ^a	116.01 ^a	59 ^a	58 ^c	646 ^{ab}	87 ^{bc}
Oxalic acid 40 mmol kg ⁻¹	1.30 ^a	2.20 ^{ab}	22.64 ^a	140.52 ^{ab}	46 ^a	45 ^{abc}	602 ^{ab}	66 ^{abc}
Tartaric acid 20 mmol kg ⁻¹	1.37 ^a	2.56 ^{ab}	21.75 ^a	155.78 ^{ab}	38 ^a	37 ^{abc}	623 ^{ab}	61 ^{abc}
Tartaric 40 mmol kg ⁻¹	1.08 ^a	2.21 ^{ab}	20.43 ^a	126.14 ^a	50 ^a	43 ^{abc}	668 ^{ab}	71 ^{abc}
Sign	**	*	***	*	*	NS	*	*

Different small letters within each column indicates significant differences among treatments at $p < 0.05$

NS Non-significant

*Significant at $p < 0.05$

**Significant at $p < 0.01$

***Significant at $p < 0.001$

control (54×10^3). As for Pb, $H_{1/2}$ at EDTA-40 exhibited a significant 6.5-fold decrease compared to the control (85×10^3 vs. 553×10^3), and Zn $H_{1/2}$ showed a similar ca. threefold decrease at EDTA-40 compared to the control (with EDTA-20 being identical to EDTA-40).

of the four studied metals (Cd, Cu, Pb, and Zn) to purslane in the treatments of the four mobilizing agents (citric acid, EDTA, oxalic acid, and tartaric acid) added in soil at 20 and 40 mmol kg⁻¹

4 Discussion

In soil, all studied PTEs exhibited an impressive increase in extractability, when the soil was amended with LMWOSs. In the case of Cd, it was EDTA-40 that caused a significant increase, while for Pb it was both EDTA-20 and EDTA-40 (Fig. 2). However, in the case of Cu and Zn,

all amended LMWOSs were successful in increasing the extractability of these metals, not only EDTA as in the case of Cd and Pb. The causation of this effect, as explained by Jalali et al. (2023), may be twofold: (a) Decreased soil pH: the naturally occurring substances are of acidic character, causing a time-limited depression of soil pH, which in turn increases cationic element availability; (b) Formation of soluble and stable organometallic complexes: Increased complexation of the added LMWOSs with the studied PTEs can lead to enhanced solubility of cationic metals in the soil solution. The former effect has indeed been well documented in the literature (e.g., Shaheen and Rinklebe 2015; Yuan et al. 2007; Ding et al. 2014). This effect is also observed in batch sorption–desorption tests, routinely reporting enhanced desorption and reduced sorption of PTEs by soil in the presence of LMWOSs (Qin et al. 2004; Najafi and Jalali 2015). As for the latter effect, the extent that PTE bioavailability increases after LMWOS addition is associated to the number of their carboxylic groups found in their structure. Citric acid bears three carboxylic groups, while tartaric, malic or oxalic acids two carboxylic groups (Suherman et al. 2019; Ding et al. 2014). However, it is not only the number of reactive groups but also their dissociation constants in relation to soil pH: If soil pH is below the negative logarithm of their dissociation constant (pK_a), then the carboxylic group is protonated, and thus inert. But if soil pH is above the given pK_a , the carboxylic group is stripped from its H^+ , hence fully reactive. Citric acid's three dissociation constants are $pK_{a1} = 3.13$, $pK_{a2} = 4.76$, and $pK_{a3} = 6.40$, while those of the oxalic acid are $pK_{a1} = 1.27$, $pK_{a2} = 4.28$, of malic acid $pK_{a1} = 3.40$ and $pK_{a2} = 5.11$, and of tartaric acid $pK_{a1} = 2.98$ and $pK_{a2} = 4.34$ (Jalali et al. 2023). This implies that in our alkaline soil, all carboxylic groups of all tested substances were fully deployed for PTE retention, thus for the formation of the organometallic complexes. EDTA, although it functions in a different way, is also known to have a pH-dependent behaviour, with its effectiveness being proportional to soil pH. In agreement with our findings, literature shows that EDTA is more potent than other, naturally occurring, substances, for increasing PTE bioavailability (e.g., as per Wu et al. 2003; Shaheen and Rinklebe 2015, reporting for Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn). The high complexation affinity of EDTA to Pb that resulted in the higher bioavailability increase compared to low molecular weight organic acids complexes with Pb that were characterized as relatively weak, was also stressed by Shaheen and Rinklebe (2015) and Shahid et al. (2012).

However, this effect is known to be short-lived: LMWOSs are readily decomposed in soil and pH values, hence PTE bioavailability, are restored back to the situation prior to LMWOS application (Macias-Benitez et al. 2020; Yin et al.

2018). For example, in a work by Macias-Benitez et al. (2020), it was reported that additions of LMWOSs up to 50 mmol kg^{-1} resulted in a pH reduction from 7.91 to 7.61 (for citric acid) and to 7.50 (for oxalic acid). In that same work it was reported that pH levels were restored back to the initial levels upon LMWOS decomposition: 50% of added LMWOSs were decomposed within only 5 days, while complete decomposition occurred 12 days after application. However, concerning EDTA, findings indicate extremely low decomposition (e.g., as per Bloem et al. 2017, who added 1500 kg EDTA ha^{-1} , equivalent to, for comparison with our work, ca. 350 mg kg^{-1} or 1.20 mmol kg^{-1}).

Purslane was chosen as a test plant due to the fact that it was previously used in other studies as a potential species for the phytoremediation of PTE-contaminated soils (e.g., Thalassinou et al. 2023 for Pb; Thalassinou et al. 2021 for Cr(VI); Levizou et al. 2016 for Cd and Zn). The contents of Cd, Pb, and Zn in purslane aerial biomass were very high in the untreated control due to the extremely high contents of these metals in soil; Cd was above 10 mg kg^{-1} in the roots at control and above 1 mg kg^{-1} in the aerial biomass. It is notable that expected contents of Cd in plants grown in non-contaminated soils is close to zero (Han et al. 2023). As for Pb, its plant contents were so high that are rarely seen anywhere in the literature. For example, in Antoniadis et al. (2021), where 12 plant species were tested for their phytoremediation capacity, no test plant achieved so high content of ca. 200 mg kg^{-1} in roots and ca. 50 mg kg^{-1} in the aerial biomass in the unamended control. Due to the fact that Pb is a non-essential element, its expected plant contents in aerial plant parts are also close to zero (Mazumder et al. 2023). The reason Pb was traced in aerial biomass is the extremely high-total Pb content in soil of 26,526.44 mg kg^{-1} . Similar to Pb, Zn extreme soil content of 17,652.63 mg kg^{-1} led to contents in plant of ca. 200 mg kg^{-1} in the aerial biomass at control, a ca. fourfold higher value from the normally expected Zn contents of ca. 40–50 mg kg^{-1} . Unlike these three metals, Cu contents in plant was rather at normal levels of less than 5 mg kg^{-1} in aerial biomass, a reflection of the metal's relatively low soil content of 181.62 mg kg^{-1} .

The added LMWOSs in this study were intended to serve as PTE-releasing agents, materials that increase the mobility of PTEs in soil. Due to the high-degradation rates of these substances, in phytoremediation projects LMWOSs should be applied when plants have developed their maximum biomass. At that point, the toxic effects to plants are limited and PTE uptake due to the increased bioavailability is maximized (Tariq et al. 2016). The addition of the four LMWOSs resulted in the increased contents of PTEs in both roots and shoots. In roots, (Fig. 1) citric acid caused an increase in Cu and Pb at 40 mmol kg^{-1} , and that of Zn at both CA-20 and CA-40. As for the aerial biomass, citric acid increased Cd at 40 mmol kg^{-1} , and, like the case of roots, it

also increased Zn at both CA-20 and CA-40 (while it failed to affect Cu and Pb in the aerial biomass). Citric acid is one of the most potent LMWOSs, known to form organometallic complexes in soil, which are readily absorbed by roots. Our findings suggest that citric acid mostly favoured Zn, as it boosted its content in purslane in both roots and shoots and in both amended rates. The formed complexes are polydentate, hence stable, yet soluble in the soil solution. As for the oxalic acid, its effect in boosting PTE contents in purslane was less pronounced: in roots it only increased Cu at 40 mmol kg⁻¹, and in aerial biomass Zn at 40 mmol kg⁻¹. In the case of the tartaric acid, it only caused an increase in root Zn at 40 mmol kg⁻¹, while in the aerial biomass it increased Zn at both 20 and 40 mmol kg⁻¹. Thus among the naturally occurring LMWOSs, the most pronounced PTE-releasing effect was recorded for citric acid, followed by the tartaric and oxalic acids. The superiority of citric acid over other tested LMWOSs was also reported by Najafi and Jalali (2015), Zhang et al. (2022), and Almaroai et al. (2012) (vs. oxalic acid), by Wang et al. (2013) (vs. tartaric, malic and oxalic acids), and by Yang et al. (2020) (vs. oxalic and acetic acids). However, not all literature data are in agreement with our findings: Nworie et al. (2017) reported that oxalic acid was more successful in boosting As, Cu, Fe, Mn, Pb, and Zn availability over citric and malic acids. On the other hand, the behaviour of EDTA, a synthetic LMWOS frequently used in phytoremediation programs for boosting PTE content, was very characteristic in the sense that it did not affect any of the metals in roots (i.e., none of them increased compared to the control when EDTA was added), while in the aerial biomass all four PTE increased significantly at both EDTA-20 and EDTA-40. Especially at EDTA-40 in the case of Cd (with a ca. fourfold increase), Pb (ca. fivefold), and Zn (ca. twofold), the increase recorded was highly notable. Thus concerning the aerial biomass, EDTA seemed to be the most successful among the amended substances in boosting PTE aerial biomass content. The impressive recorded efficiency of EDTA to cause a fivefold increase in aerial tissue Pb content, as well as Cd, Cu, and Zn, has been previously reported in the literature (Chen et al. 2022; Macias-Benitez et al. 2020; Shinta et al. 2021; Gul et al. 2020). However, despite the increased ability of EDTA for PTEs, an effect that could lead to increased phytoremediation potential for a series of cationic elements, the low-degradation rates of EDTA may lead to increased PTE bioavailability for unpredictable long periods of time. This could cause environmental concerns associated with PTE leaching to ground water bodies or with undesirable uptake by a range soil organisms (Nascimento et al. 2021). In parallel to the increased availability of cationic elements after low-molecular weight organic acid application, increased activity of Zn/Fe transporters was noticed for the species *Oryza sativa*, leading to increased absorption of Mn²⁺, Fe²⁺, Cd²⁺, Co²⁺, Ni²⁺ and

Zn²⁺ (Yang et al. 2022). However, for the LMWOSs exhibiting high rate of decomposition in soil (i.e., the naturally occurring substances), the increased bioavailability of PTEs is rather temporal (Macias-Benitez et al. 2020).

In contrast to EDTA, the naturally occurring substances are found in soil as a result of the decomposition of organic matter or as root exudates when there is an imbalance in the plant uptake of anions vs. cations from the soil solution (Jones 1998). When uptake of cations in equivalent mass (i.e., in mEq per mass soil or per volume of soil solution) surpasses that of anions, plants counter-balance this unstable situation by eluting back to soil substances functioning as the equivalent of proton (H⁺), i.e., organic substances of low-molecular weight of acidic reaction (Wang et al. 2013; Naidu and Harter 1998). Most usual such substances include, apart from the three used here, malic, fumaric, and succinic acids (Kozdroj and van Eisas 2000).

Although the amendment of the releasing agents resulted in increased PTE contents in purslane, its growth parameters (height and dry biomass of stems, leaves and roots; Table 1) did not seem to be affected negatively, due to the fact that plants have certain defence mechanisms against PTE exposure (Narayanan and Ma 2023). This suggests that the beneficial effects of the absorbed substances overcame any possible negative effects of boosted PTE contents, a finding also agreed by Thalassinou et al. (2023), in a work where the toxic effects of elevated added Pb to purslane was masked by generous additions of N, which boosted plant vigor. Plant height and tissue dry weight were not negatively affected by the LMWOS application. The absence of negative effects on plant growth could be attributed to the fact that metals often conjugate with low molecular weight organic acids and synthetic chelates that result in promoting the transport of complexed metal into the vacuole (Pinto and Ferreira 2015; Osmolovskaya et al. 2018; Sabir et al. 2014; Han et al. 2018; Zhang et al. 2018).

All the same, there seems to be a downside of the boosted plant uptake of PTEs: It can lead to limited uptake of nutrients from plants (as per Gul et al. 2020, who referred to Na, Ca, K, P, Mg, Zn, Fe, and Cu). YSL transporters mediate Ni, Zn, Cd, Mn, and Cu besides Fe transport. Especially for elements such as Cd and Zn, due to their similar physicochemical characteristics, common intake pathways are possible (Yang et al. 2022). Furthermore, high contents of Zn, Cd, Co, Ni, and Mn may significantly reduce Fe uptake from IRT1 transporter, and in many cases Fe low contents in plant tissues are accompanied with high Zn and Cd contents (Lešková et al. 2017). Similarly, Mn, Cd, and Zn contents may significantly affect Fe uptake due to the low selectivity of NRAMP and ZIP transporters (Fan et al. 2018). For plant species *Arabidopsis thaliana* and *Populus glauca* grown under Cd stress, limited Fe uptake was found to have led to Fe deficiency symptoms that were alleviated upon Fe

supply (Solti et al. 2008; Hermans et al. 2011). In this work, however, Fe uptake did not seem to be significantly affected (data not shown).

Although added LMWOSs caused the aforementioned increase in plant PTE contents, the TC of any metal was found to fall far short from satisfying the criterion of approaching the unity (Table 2). Although TC values of all metals increased in most LMWOS additions, especially at EDTA-20 and EDTA-40, they were at least one order of magnitude lower than unity. There are two possible reasons for this behaviour: First, TC is associated with the total levels of soil PTEs: Although plant content increases with soil content, this increase is never linear; it is rather exponential, heading towards a “plant saturation” plateau as soil PTE contents increase, causing a decrease in TC at very high soil PTE levels (Levizou et al. 2016; Antoniadis et al. 2017). Thus at extreme soil PTE enrichment, such as the case here, TC cannot be expected to have a value anywhere close to unity. Second, the requirement of such high TC values are often dictated by, and is often found in, works where PTE are spiked to soil just prior to the commencement of the experimentation. In such cases, PTEs are highly mobile and are frequently found to cause plant toxicities (Thalassinos et al. 2023). However, in cases where PTEs have been deposited over long periods of time of centuries or even millennia (such as the case in our work), PTEs are expected to be gradually transferred to inactive and residual soil pools—an effect known as “PTE ageing” (Antoniadis et al. 2017). As for the TF, the requirement for a $TF > 1.0$ for a plant to be characterized as hyperaccumulator, was indeed achieved for Pb and Zn in the EDTA treatments: for Pb at EDTA-40 (1.014) and for Zn at EDTA-20 (1.670) and EDTA-40 (2.017) (Table 2). Such high values have previously been reported for *Artemisia vulgaris* (Antoniadis et al. 2021), but tested plants in that work were grown in a soil with a lot lower total soil PTE contents than in our study.

Although TC and TF are the main requirements for plants to be characterized as suitable species for phytoremediation, they have a certain shortcoming: they are solely content-related. However, our data suggest that there is a highly important “hidden” restrictive factor that is often overlooked: the produced plant biomass able to be harvested and taken away from the contaminated area. This was recorded in our case with uptake, an index incorporating, apart from content, plant biomass as well (Table 3). This analysis exhibited rather bluntly the apparent failure of the process of phytoremediation, especially in our soil with extremely high PTE soil levels: The number of harvests required to reduce soil content to half was beyond any consideration of practical applicability. This was evident even in the cases of Zn and Pb when added with EDTA, a treatment seemingly successful for these two metals concerning TF. The vast number of required harvests indicates the degree of

the problem regarding scalability to real-field conditions; remediation solutions need to have a foreseeable horizon in time into which a viable ecosystem restoration concerning decreased contamination may be achieved—but this seems to fail as an ambition concerning phytoremediation. It also indicates a problem concerning the economic viability: the application of EDTA or other LMWOSs as a sprayed solution at field scale at rates such as those applied here (even if taken at 20 mmol substance kg^{-1} soil) would mean the necessity of the application of 23.4 t of EDTA ha^{-1} —merely the cost of purchase of the substance would be in the area of half a million euros per hectare. Moreover, the possible longevity of added EDTA to soil may be undesirable, as it may result in secondary environmental burdens before EDTA is decomposed in soil: possible toxic effects of EDTA added at high doses should not be ruled out. This unwanted effect, as well as a possible leachability and persistent mobilization of PTEs with the chelates, especially synthetic like EDTA, may constitute a major drawback concerning its universal applicability (Zuluaga et al. 2023). Lastly, it also shows that it is far more practically viable for highly polluted soils to have a paradigm shift towards ecosystem phytomanagement rather than phytoremediation when dealing with ecosystem management. Phytomanagement would not aim at cleaning soils from PTEs with the use of cultivated plants, but rather to achieve high plant biomass yields of non-food plants. This is a more conservative management practice that would give sufficient income for the producers, and produced biomass would be targeting uses of industrial interest—a process that would also reduce the need for primary natural resources, as plant materials are considered as recycled matter.

5 Conclusions

In a soil with extremely high contents of Cd, Pb, and Zn, but mildly elevated in Cu, low-molecular-weight organic substances (LMWOSs), both of natural occurrence (citric, oxalic, and tartaric acids) and synthetic (EDTA), were amended to soil to facilitate PTE phytoextraction by purslane (*Portulaca oleracea*). In the case of Cd and Pb, soil extractability was increased only with added EDTA, while for the other two metals all added LMWOSs were successful in increasing their extractability. At plant level, added LMWOSs increased the aerial biomass contents of all PTEs at EDTA, while in the case of Zn all added LMWOSs were successful. Also the PTE root-to-shoot translocation was found to be higher than unity for Pb and Zn in the treatment of EDTA. Although such results seem to be promising, when “PTE uptake” (in units of PTE mass in plant per pot—an index incorporating plant biomass apart from soil and plant contents alone) was recorded, the shortcomings of the phytoremediation process were exhibited. Based on uptake, the

harvests needed to reduce the dramatically high soil PTE contents to half were found to be beyond any practical consideration. Based on these findings, we come to a conclusion that bears significant environmental implications: There needs to be a paradigm shift in our demands of soils being cleaned from PTEs via phytoextraction, when soil PTE content is dramatically elevated, such as in the case of our study. Even if plants seem to achieve certain content-based criteria, such as those of TC and TF approaching or surpassing unity, the process may still be practically impossible. Instead, there should be an approach of acquiring *phytomanagement*, a much more viable process that generates income for producers and recycled plant biomass-based materials for certain biobased industrial valorization pathways. We consider this work as a first attempt to address this much needed paradigm shift; more research is certainly needed under real-field conditions and with the use of more plant species, soil improvers that would tend to stabilize, rather than release, soil PTEs, especially in soils dramatically elevated with such pollutants. Also tests should be conducted in soils with varying properties so that soil geochemical processes of PTEs may be better elucidated.

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Data Availability Data sets generated during the current study are available from the corresponding author upon request.

Declarations

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest. The authors have no relevant financial or non-financial interests to disclose.

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