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An Integrated Approach to Remediate Saline Soils and Mining Waste Using Technosols and Pasture Development

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Abstract: Reclaiming marginal lands such as saline soils or mining waste for livestock grazing through Technosols and phytostabilisation can provide a solution to the growing food demand. This study evaluated the enhancement of soil properties by two Technosol constructions, along with pasture development. The experimental set-up consisted of gossan waste (G), Fluvisol (VF), Technosol/gossan (TG), and Technosol/Fluvisol (TVF), both Technosols consisting of G and VF, respectively, mixed with organic and inorganic amendments. These substrates were sown in pasture in pots (1.5 dm^3) that was cut one and two months after sowing to simulate grazing. Both Technosols improved soils properties, with the acidity of G neutralising in TG. Yet, in TVF, a 65% reduction in salinity and a 60% drop in exchangeable Na occurred compared with VF. Nutrient pool, aggregate stability, and microbiological activity were also improved. Dehydrogenase activity was practically 0 in G, while in TG it was 15 times higher, and with pasture it increased 6-fold. In FV, some activity was already present, but in TVF it was six times higher and even increased with pasture. Finally, these improvements allowed the establishment of a healthy pasture, with twice the biomass and less accumulation of potentially hazardous elements in TG, and considerable growth in TVF. Thus, the co-application of Technosols and pasture may be effective in converting marginal lands into productive areas (grazing, foraging, biomass energy).

Keywords: salinity; potentially hazardous elements (PHEs); acidity; gossan waste; marginal lands; mine reclamation; feed production; soil enzymes; ecotoxicity assessment; engineered soils

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1. Introduction

Soil degradation is a major threat to humanity as it compromises the continued availability of food for a growing world population and undermines ongoing efforts to avoid the loss of species and ecosystems and the negative consequences of global climate change [1]. The main causes and, consequently, threats to its ecological functions are erosion, organic matter depletion, biodiversity loss, compaction, sealing, contamination, and salinisation/sodification [2]. This work focuses on contamination, with more than five million sites affected by potentially hazardous elements (PHEs) mainly due to mining activity [3], and salinisation affecting over 480,000 ha of fertile soils due to natural (e.g., intertidal zones or marine sediment deposition) [4] or human-induced processes (e.g., freshwater aquifer overexploitation or irrigation with low-quality water) [5]. Moreover, in the coming years, as the demand for food will increase significantly along with population growth, agricultural land will become a limited and strained resource. It is therefore crucial to ensure a highly productive and sustainable agricultural system.

In this context, the reclamation of unused marginal lands, such as saline and drought-prone lands, or even abandoned mining areas, may constitute a possible strategy [6,7]. To this end, phytostabilisation is considered an appropriate method for their rehabilitation and reconversion to agricultural and livestock activities. For example, some pasture plants (e.g., grasses, legumes) can tolerate adverse growing conditions, such as high concentrations of PHEs and electrical conductivity (EC), low pH, organic C and nutrients, and poor structure. Indeed, legume and grass species of genera such as *Lolium* sp., *Trifolium* sp., and *Medicago* sp., common in pastures, have been described as potential candidates for phytostabilisation [8,9]. However, under these conditions plant growth is often limited and slow, thereby constraining the environmental rehabilitation success. For this reason, phytostabilisation has been commonly combined with the application of amendments that promote different biogeochemical and edaphic processes, leading to an improvement in soil properties and a more persistent decrease in PHE mobility and availability, providing favourable conditions for plant and soil microbiota growth [10]. In this sense, the integrated application of specific amendments with different properties is recommended to maximise their use efficiency [11,12], as the impact of some amendments can be weak in the long term [13,14], requiring successive applications that increase remediation costs [15]. Because of this, different and complementary amendments have recently been applied in combination to produce specific and designed soils (Technosols [16]) that maximise and prolong the effects of amendments over time [14,17].

Technosols consist of engineered soils specifically designed for a specific environmental problem (commonly referred to as Technosol "a la carte" or tailor-made Technosol [13]), and are characterised by their technical origin in terms of properties and pedogenesis [16]. Indeed, most Technosols applied in soil remediation programmes are made from waste, as this ecotechnology also tackles unsustainable waste generation. In addition to improving basic soil functions, Technosols favour various biogeochemical and edaphic processes such as acid neutralisation, decrease in sulphide oxidation, immobilisation of PHEs, improvement in soil fertility, and stimulation of soil biological activity due to the complementarity of their components, contributing to the medium- and long-term sustainability of the remediation process [18,19]. Previous studies of different Technosols in combination with plant cultivation, both in microcosm studies under controlled conditions [19–28] and in large-scale interventions [17,29–33], have proven the effectiveness of this ecotechnology for the remediation of both mining and salinity-affected areas.

Therefore, this study aims to assess the potential of an ecotechnology based on Technosols and phytostabilisation that combines pasture growth on two designed Technosols derived from gossan waste and a saline soil, respectively, for the remediation of these marginal lands. In particular, the objective is to promote favourable conditions in the gossan waste and saline soil for optimal growth of a pasture (e.g., enhance physicochemical properties, aggregate stability and microbiological activity, and decrease PHE bioavailability), and to evaluate the safety of animal consumption of this pasture in order to dedicate these remediated areas for livestock grazing.

2. Materials and Methods

2.1. Study Areas

Two sites in Portugal were considered for this study: an abandoned mining area contaminated by potentially hazardous elements (PHEs) at the São Domingos mine, and an abandoned and degraded estuarine area affected by salinity, the "Praia do Sobralinho" in the Tagus Estuary. Climate is typically Mediterranean (semi-arid mesothermic, Thornthwaite classification).

The São Domingos mine is sited in the northern sector of the Iberian Pyrite Belt (37°40′28″ N, 7°30′01″ W) and is considered one of the largest historical mining sites in operation since pre-Roman times, with the extraction of Au, Ag, and Cu, that ceased in the 1960s [34]. In this later period, mining focused on Cu, S, Au, Pb, and Zn in both gossan and massive sulphides [35], producing large amounts of mining waste scattered, irregularly, along the mine area [34]. This mining waste presents chemical characteristics that pose a high environmental risk [34,36].

The fluvial area of the "Praia do Sobralinho" is located in the Municipal Council of Vila Franca de Xira (38°54′16″ N, 9°01′09″ W), integrated in the metropolitan area of Lisbon, on the west coast of Portugal, where the salt tide reaches about 50 km upstream from the river mouth [25].

2.2. Experimental Setup

The microcosm assay consisted of four treatments (hereafter, substrates) set up in pots of approximately 1.5 dm^3 volume in four replicates. The substrates were (i) gossan waste from the São Domingos mine (GW), control of PHE-contamination, (ii) gossan composite Technosol (TG), (iii) salic Fluvisol (Eutric) [16] from the Sobralinho salt marsh area (VF), control of salinity affection, and (iv) Technosol composed of saline Fluvisol (TVF). TG was produced with 95% GW and 5% (by mass) waste mixture consisting of biomass pruning, gravel limestone (Ø < 5 mm), coffee grounds, sludge, and waste kieselguhr from breweries at a ratio of 25:20:20:25:10; and TVF with 85% VF and 15% waste (by mass) mixture composed of sludge and waste kieselguhr from breweries, medium sand (0.25–0.5 mm), gravel limestone (2 mm < Ø < 5 mm), and biomass pruning at a ratio of 15:5:30:20:30. The characterisation of the wastes is available in [24,25]. All substrates were incubated at 75% of water-holding capacity and room temperature (20–25 °C) for 30 days. These substrates were used for growing *Limonium daveaui* Erben (unpublished data) for 6 months and, after plant collection, the substrates were left bare for 15 months and then 5 g of seed mix per pot and substrate was sown. The seed mixture was composed of pasture species such as legumes (*Trifolium* sp. [*T. michelianum* var. *paradana* Savi, *T. vesiculosum* var. *cefala* Savi, *T. resupinatum* var. *nitrofolus* L., and *T. squarrosum* L.] and *Medicago* sp.) and grasses (*Lolium multiflorum* Lam). On the sowing day (23 September 2021), a composite sample (five subsamples) of the substrates per pot was collected, hereafter referred to by initial (G_i, TG_i, VF_i, TVF_i). After one month of growth (25 October 2021), the pasture biomass generated so far was mown to simulate livestock grazing (1st cut). Subsequently, after two months (25 November 2021), a final cut was applied to simulate grazing (2nd cut). In this case, in addition to shoots, roots were also collected, and again a composite sample (five subsamples) of the substrates per pot, hereafter referred to as final (G_f, TG_f, VF_f, TVF_f). The complete assay was carried out in a greenhouse under natural sunlight and controlled aeration conditions with the substrates kept at 75% of water-holding capacity. After sampling, an aliquot of each substrate was stored at 4 °C in sterile opaque cold-preserved bottles for the analysis of soil enzymatic activities. The remaining part of the sampled substrate was air-dried at room temperature, homogenised, and sieved to 2 mm for physicochemical characterisation and determination of PHE concentrations.

2.3. Sample Analysis

The following physicochemical characterisations of all substrates (G, TG, VF, and TVF) both at the beginning and at the end of the experiment were carried out according to [37]: pH and electrical conductivity (EC) in water suspension (1:2.5 m/V), total organic C (C_{org}) by wet combustion, total N (N_T) using the Kjeldahl method, and extractable P and K (P_{Ext} and K_{Ext}) by the Egner–Riehm method. Total concentrations of macro- (Ca, Mg, Na, K) and micronutrients (Fe, Mn, Zn and Cu) were also analysed by flame atomic absorption spectroscopy after extraction by the Lakanen and Erviö method [38]. The concentrations of PHEs (As, Cu, Ni, Pb, Sb, S, Zn) in the bioavailable fraction of all substrates were measured by inductively coupled plasma mass spectrometry (ICP-MS) in Activation Laboratories Lda. [39,40] after extraction by the rhizosphere-based method [41], which consisted of mixing 3 g of moist rhizosphere soil with 20 mL of a combined organic acid solution of acetic, lactic, citric, malic, and formic acids. The soil aggregates' distribution in the final samples was also measured by determining the percentage of each particle size fraction by sieving the aggregates/particles > 0.05 mm through a column of five sieves with different mesh sizes (1, 0.5, 0.2, 0.1, and 0.05 mm) after immersion of the non-disturbed samples in

96% (V/V) ethanol [42]. Soil fractions (1–2; 1–0.5; 0.5–0.2; 0.2–0.1; 0.1–0.05 mm) were then weighted; fraction < 0.05 mm was estimated by difference.

The enzymatic activities were analysed on all substrates as biological indicators to assess the remediation process. As such, dehydrogenase [43] was used as an index of overall microbial activity [44,45], while β-glucosidase [46], acid phosphatase [47], and urease [48] were associated with C, P, and N cycles [49–51], respectively. Cellulase that was linked to the C-cycle [52] was also determined according to [52,53], along with protease activity [54], which included several enzymes that catalysed the hydrolysis of proteins and oligopeptides to amino acids involved in the N-cycle [55].

Plant shoots from the first and second cut samples, and the root samples from the end of the assay, were washed with tap water followed by distilled water; roots were also sonicated (after washing) in distilled water in an ultrasound bath for 30 min. Shoots and roots were dried at 40 °C, weighed for dry weight, and finally homogenised into a fine powder. For each substrate, PHEs and nutrients accumulated in shoots were determined by ICP-MS in Activation Laboratories Lda. after digestion (HNO_3) [39,40].

Activation Laboratories Lda. is a certified laboratory [56]; thus, quality control of the multi-elemental analyses of substrates and plant samples was performed by Activation Laboratories' standards. Quality control of the remaining analyses was carried out by technical replicates, the use of certified standard solutions, and method reagent blanks.

2.4. Data Analysis

Previous to the statistical treatment of the data, the normal distribution test (Kolmogorov–Smirnov) and the homogeneity of variances test (Levene) were performed. As normality and/or homogeneity of variances were not met, non-parametric tests (Kruskal–Wallis and Mann–Whitney U) ($p < 0.05$) were used. All statistical analyses were made with a confidence level of 95% using RStudio software V. 2023.06.0 "Mountain Hydrangea" (RStudio Inc., 250 Northern Ave, Boston, MA, USA).

3. Results and Discussion

3.1. Physicochemical Characterisations of Gossan Waste, Salt-Affected Fluvisol, and Technosols

The gossan waste from the São Domingos mining area (G) constituted a degraded environment like most wastes from sulphide mining areas, as it showed extreme acidity (pH ~ 3.8) and very low fertility, manifested by very low contents of organic C (4 g kg^{-1}), total N (0.16 g kg^{-1}), extractable P (0.56 mg kg^{-1}), and K (37.5 mg kg^{-1}) (Table 1), along with very low concentrations of macro- and micronutrients (in mg kg^{-1}; Mg: 30, Mn: 1) and moderate levels of Fe (29 mg kg^{-1}), Cu (2 mg kg^{-1}), and Zn (3 mg kg^{-1}) (Table 2) [57]. A high ratio of Ca/Mg (>8.0) indicates poor nutritional conditions for plants [57]. The gossan waste contained high total concentrations of PHEs (in g kg^{-1}; As: 9.13, Cu: 0.22, Hg: 0.03, Pb: 29.63, Zn: 0.08) (Table A1) [58], and relatively high bioavailable concentrations of some PHEs such as Pb (5.5 mg kg^{-1}) and S (650 mg kg^{-1}) (Table 3). These waste materials had total concentrations of As, Cu, Hg, and Pb exceeding 830, 3.5, 169, and 658 times, respectively, the most restrictive regulatory level (usually for agricultural use) [59,60]; thus, they can be considered contaminated by these PHEs for agricultural, residential/parkland, commercial, and industrial uses. In fact, they may pose a risk to the environment and human health (e.g., cardiovascular diseases, cancers, imbalance of soil fauna and flora, food chain toxicity) due to the bioavailability of PHEs and the consequent long-term adverse effect of their release [61,62].

Table 1. Physicochemical characteristics of the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF) (mean ± SD, $n = 4$).

Physicochemical Characteristics	**G**		**TG**		**VF**		**TVF**	
	Initial	**Final**	**Initial**	**Final**	**Initial**	**Final**	**Initial**	**Final**
pH (H_2O)	3.80 ± 0.04 aA	4.08 ± 0.09 aB	6.53 ± 0.23 b	6.70 ± 0.13 b	8.26 ± 0.07 A	8.52 ± 0.05 B	8.46 ± 0.13 A	8.89 ± 0.11 B
EC (dS m^{-1})	0.70 ± 0.17 aB	0.12 ± 0.02 aA	1.33 ± 0.30 bB	0.32 ± 0.14 bA	11.20 ± 1.52 bB	0.83 ± 0.11 A	3.96 ± 1.20 aB	0.64 ± 0.45 A
C_{org} (g kg^{-1})	4.22 ± 0.74 a	5.41 ± 1.77 a	9.23 ± 1.24 bA	14.18 ± 2.50 bB	18.87 ± 1.36 a	19.43 ± 0.72 a	28.15 ± 0.67 b	28.13 ± 1.30 b
N_T (g kg^{-1})	0.16 ± 0.01 aA	0.27 ± 0.02 aB	1.18 ± 0.20 bB	0.70 ± 0.22 bA	1.65 ± 0.05 aA	1.81 ± 0.10 aB	2.73 ± 0.17 b	2.48 ± 0.13 b
P_{Ext} (mg kg^{-1})	0.56 ± 0.68 a	bdl a	55.97 ± 8.02 b	46.72 ± 9.94 b	92.69 ± 2.19 a	98.04 ± 2.77 a	424.29 ± 27.35 b	425.33 ± 43.02 b
K_{Ext} (mg kg^{-1})	37.49 ± 17.30 a	22.95 ± 6.21	153.81 ± 25.13 bB	23.63 ± 2.50 A	799.29 ± 29.89 a	811.77 ± 24.34	942.85 ± 38.58 bB	844.44 ± 54.21 A

SD—standard deviation, EC—electric conductivity; C_{org}—organic carbon; N_T—total nitrogen; P_{Ext}—extractable phosphorus; K_{Ext}—extractable potassium, bdl—below detection limit. Lower-case letters indicate significant differences between the control (G or VF) and the respective Technosol (TG or TVF) at each time; and capital letters indicate significant differences in each treatment with respect to time (beginning and end of pasture cultivation) (U test Mann–Whitney).

Table 2. Total concentration of macro- (Ca, Mg, Na, and K) and micronutrients (Cu, Fe, Mn, and Zn) in g kg^{-1} present in the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF) (mean ± SD, $n = 4$).

Elements (g kg^{-1})	**G**		**TG**		**VF**		**TVF**	
	Initial	**Final**	**Initial**	**Final**	**Initial**	**Final**	**Initial**	**Final**
Ca	0.38 ± 0.05 aB	0.06 ± 0.02 aA	2.25 ± 0.69 bB	1.04 ± 0.54 bA	4.04 ± 0.29 a	3.23 ± 0.55 a	8.61 ± 0.84 b	7.85 ± 2.90 b
Mg	0.03 ± 0.01 aB	0.01 ± 0.01 aA	0.07 ± 0.01 bB	0.02 ± 0.01 bA	2.25 ± 0.28 bB	1.57 ± 0.07 A	1.66 ± 0.09 aB	1.49 ± 0.06 A
Na	0.11 ± 0.04 B	0.05 ± 0.01 A	0.24 ± 0.17	0.09 ± 0.04	11.15 ± 2.64 bB	5.36 ± 1.15 bA	4.44 ± 2.08 aB	2.25 ± 0.42 aA
K	0.03 ± 0.01 a	0.02 ± 0.01	0.16 ± 0.02 bB	0.02 ± 0.00 A	0.78 ± 0.03 a	0.77 ± 0.02	0.99 ± 0.07 bB	0.82 ± 0.05 A
Cu	0.002 ± 0.001 aA	0.006 ± 0.001 aB	0.006 ± 0.001 bA	0.009 ± 0.001 bB	0.007 ± 0.000 aA	0.011 ± 0.001 aB	0.010 ± 0.000 bA	0.014 ± 0.001 bB
Fe	0.029 ± 0.002 aA	0.044 ± 0.006 aB	0.145 ± 0.015 bB	0.125 ± 0.006 bA	0.148 ± 0.003 aA	0.175 ± 0.022 aB	0.566 ± 0.025 bB	0.495 ± 0.034 bA
Mn	0.001 ± 0.001 a	0.000 ± 0.000 a	0.003 ± 0.001 bB	0.001 ± 0.001 bA	0.288 ± 0.009 b	0.282 ± 0.017 b	0.242 ± 0.006 aB	0.221 ± 0.009 aA
Zn	0.003 ± 0.001 a	0.003 ± 0.001 a	0.006 ± 0.001 b	0.006 ± 0.001 b	0.011 ± 0.001 aA	0.014 ± 0.002 aB	0.018 ± 0.001 bA	0.020 ± 0.001 bB

SD—standard deviation. Lower-case letters indicate significant differences between the control (G or VF) and the respective Technosol (TG or TVF) at each time; and capital letters indicate significant differences in each treatment with respect to time (beginning and end of pasture cultivation) (U test Mann–Whitney).

Table 3. Available concentrations of potentially hazardous elements (PHEs) in mg kg^{-1} present in the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF) (mean ± SD, *n* = 4).

Elements (mg kg^{-1})	**G**		**TG**		**VF**		**TVF**	
	Initial	**Final**	**Initial**	**Final**	**Initial**	**Final**	**Initial**	**Final**
As	0.15 ± 0.17 a	bdl	3.89 ± 0.16 b	4.10 ± 0.24	0.15 ± 0.17 aA	0.45 ± 0.06 B	0.48 ± 0.05 b	0.45 ± 0.13
Cu	1.05 ± 0.13	0.90 ± 0.07 b	0.76 ± 0.29	0.71 ± 0.02 a	0.21 ± 0.02	0.25 ± 0.03	0.26 ± 0.04	0.26 ± 0.03
Ni	0.14 ± 0.02 a	0.15 ± 0.05	0.20 ± 0.04 bB	0.11 ± 0.02 A	0.18 ± 0.04	0.21 ± 0.07	0.16 ± 0.05	0.14 ± 0.03
Pb	5.48 ± 1.27 b	6.01 ± 0.59 b	0.95 ± 0.95 a	0.88 ± 0.29 a	bdl	bdl	bdl	bdl
Sb	0.23 ± 0.05	0.20 ± 0.00	0.20 ± 0.00	0.23 ± 0.05	0.10 ± 0.12	0.18 ± 0.13	bdl	bdl
S	647.56 ± 13.26 B	162.08 ± 19.18 A	907.58 ± 214.50 B	197.21 ± 69.89 A	792.24 ± 322.77 B	239.53 ± 53.58 bA	428.45 ± 191.97 B	132.11 ± 35.52 aA
Zn	3.05 ± 0.52 B	1.94 ± 0.21 aA	3.70 ± 1.07	3.80 ± 0.23 b	0.49 ± 0.08 b	0.56 ± 0.04 b	0.36 ± 0.06 a	0.35 ± 0.05 a

SD—standard deviation, bdl—below detection limit. Lower-case letters indicate significant differences between the control (G or VF) and the respective Technosol (TG or TVF) at each time; and capital letters indicate significant differences in each treatment with respect to time (beginning and end of pasture cultivation) (U test Mann–Whitney).

The salic Fluvisol (Eutric) from the Sobralinho salt marsh area (VF) also showed adverse physicochemical characteristics. It was slightly alkaline (pH 8.2) and saline (EC > 11 dS m^{-1}), with low-medium contents of organic C (19 g kg^{-1}) and total N (1.6 g kg^{-1}), and high contents of extractable P (92.7 mg kg^{-1}) and extractable K (0.8 g kg^{-1}) (Table 1) [57]. According to the classification of Portuguese soils [57], the concentrations of micronutrients were very high for Fe, Mn, and Zn, but medium for Cu, and all the macronutrient concentrations were very high. Despite the high macro- and micronutrient concentrations, the saline/sodic Fluvisol was not very fertile, with almost 25% exchangeable Na [25]. A high quantity of exchangeable Na contributes to the degradation of soil aggregates and the dispersion of colloids, favouring the obstruction of soil pores and hindering root penetration of both non-succulent and succulent plants, as previously observed in other studies [25,26]. In this respect, the [Ca]/[Mg] ratio of 1.79 (Table 2) suggests very adverse conditions for the soil physical properties [57]. Total concentrations of PHEs in VF (Table A1) were below the maximum permissible values for agricultural use, except for As, at concentrations slightly above the limit of 11 mg kg^{-1} [59,60]. Similarly, the PHE concentrations in the bioavailable fraction were not high, except for S, which was slightly high (Table 3).

Therefore, both gossan waste and salt-affected soil present unfavourable conditions that need to be restored. In addition to the general improvements required, such as increasing nutrient availability and organic C content, and improving structure and water-holding capacity, which are essential for rehabilitation in drought-prone areas such as these [63], the specific problems of acidity and PHE toxicity in gossan waste and salinity in saline Fluvisol need to be addressed. For this, the addition of amendments has been widely used [63,64], although some of these effects may not last over time [10,11]. So, developing specific Technosols adjusted to the particular conditions of each degraded environment by mixing amendments for a better promotion and maintenance of biogeochemical processes and a better decrease in PHE bioavailability to plants can be more efficient [10,11].

The ecotechnology of Technosols significantly improved physicochemical properties and nutritional status (Tables 1 and 2), mitigating the main disturbances of gossan waste and saline soils. In TG, the extreme acidity of the gossan waste was neutralised by increasing pH in 2.7 units due to the incorporation of limestone rock wastes that provide acidity buffering capacity [24,25]. Similarly, salinity (EC) and exchangeable Na of the saline Fluvisol were reduced by about 65% and 60% in TVF, respectively. This reduction was due to the substitution of Na^+ for Ca^+ in the exchange complex (Table 2), which is a vital process for the remediation of saline/sodic soils [64]. For this reason, gypsum-based amendments have been commonly employed in the remediation of these degraded soils, as it causes the formation of Na_2SO_4 that can be leached [65]. However, as seen in TVF, engineered soils composed of carbonated and organic wastes can be used as an alternative to improve the properties of soils affected by salts [66,67]. In both Technosols, the nutrient pool was also enhanced due to the incorporation of organic amendments (biomass pruning, coffee grounds, sludge, and waste kieselguhr) with high levels of organic C, total N, extractable P and K, among others [24,25]. The increase was much more pronounced in TG than in TVF, as the fertility conditions of G were worse than in VF. In TG, organic C doubled, total N increased 7.4-fold, extractable P increased 100-fold, and extractable K increased 4-fold compared with G, while, in TVF, these contents were 1.5, 1.6, 4.6, and 1.2 times higher than in VF, respectively (Table 1). Similarly, most of the extractable macro- and micronutrient concentrations increased significantly in both Technosols, particularly Ca, Fe, Zn, and Cu in TG, and Ca and Fe in TVF (Table 2).

The bioavailability of PHEs in Technosols, compared with G_i and VF_i, experienced element-dependent variations, mainly driven by increasing organic C and pH [68,69]. In TG, some PHEs such as Ni, Sb, and Zn remained at concentrations similar to G, but Pb was strongly diminished by 80% and Cu to a lesser extent (28%), while As was increased by up to 26 times. Thus, as found in previous studies [17,70,71], in the bioavailable fraction, As increased whereas Pb decreased. Indeed, an increase in organic C can reduce the mobility/bioavailability of Pb and increase the bioavailability of other PHEs like As.

Furthermore, when the pH is higher than 6.5 in non- or low-carbonated soils such as the studied Technosols, As bioavailability increases, as this element can be desorbed from iron oxides and organic matter [72–74]. The observed increase in As bioavailability can also be attributed to the increase in extractable P concentration (Table 1) in Technosols [17], since phosphate anions can compete with As anions for binding sites in soil components, resulting in As bioavailability increase [75], whereas, in TVF, there was almost no change in the low bioavailable concentrations of most PHEs, apart from the decrease in Sb to values below the detection limit and the non-statistically significant decrease in S (Table 3).

Throughout the vegetative growth of pasture, the physicochemical characteristics, nutrient content, and PHE concentrations in their bioavailable fractions of all substrates experienced variations (Tables 1–3). In this sense, over time, a decrease in EC was observed in all substrates, although this was probably largely due to irrigation rather than pasture cultivation. Organic C content also increased with pasture growth, although only statistically significantly in TG, with an increase of about 54%. In TG, N_T and K_{Ext} contents decreased significantly with pasture growth, while, in the other substrates, these variations were not as significant. Generally, in all substrates, most nutrient concentrations were higher before pasture growth. Also noteworthy was the decrease in Na in TVF after pasture cultivation, and the decrease in S bioavailable concentrations in all substrates.

The effect of Technosols was not limited to physicochemical properties, nutritional status, or bioavailable concentrations of PHEs. The addition of amendments influenced the poor physical properties of initial soils. Improved aggregation was observed in both Technosols, as the number of larger aggregates (>2 mm) was higher than in the degraded materials. In TG, this class of aggregates represented 68% compared with 34.5% in G, and in TVF they accounted for 93.6% compared with 32.8% in VF (Table 4).

Table 4. Aggregates' distribution (% of each fraction in relation to the total) in the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF) at the end of pasture cultivation (mean ± SD, *n* = 4).

Aggregates' Distribution (%)	G	TG	VF	TVF
>2 mm	34.53 ± 5.44 a	67.98 ± 3.50 b	73.76 ± 10.43 a	93.56 ± 0.50 b
1–2 mm	15.05 ± 2.91 b	7.69 ± 1.35 a	10.01 ± 4.61 b	1.04 ± 0.29 a
0.5–1 mm	15.19 ± 1.20 b	7.78 ± 0.93 a	6.81 ± 3.41 b	0.68 ± 0.23 a
0.2–0.5 mm	13.32 ± 1.84 b	6.56 ± 1.68 a	3.94 ± 2.01 b	0.41 ± 0.12 a
0.1–0.2 mm	10.79 ± 1.25 b	5.15 ± 1.15 a	1.84 ± 0.87 b	0.20 ± 0.04 a
0.05–0.1 mm	5.78 ± 0.62 b	2.56 ± 0.19 a	0.50 ± 0.23 b	0.05 ± 0.01 a
<0.05 mm	5.34 ± 1.09 b	2.29 ± 0.55 a	3.15 ± 0.83	4.07 ± 0.19

SD—standard deviation. Lower-case letters indicate significant differences between the control (G or VF) and the respective Technosol (TG or TVF) (U test Mann–Whitney).

3.2. Biological Characterisations of Gossan Waste, Satl-Affected Fluvisol, and Technosols

To assess the remediation effectiveness of Technosols, the enzymatic activities were used as bioindicators of the microbiological activity, because they indicated the soil functional diversity and the changes in the composition of the microbial community and the microbial status [45,76]. Enzymatic activity in gossan waste (G) was very low, registering the lowest values at baseline for all the studied enzymes (except acid phosphatase) (Figure 1). In saline Fluvisol (VF), enzymatic activity was not as low as in G, but it was at levels considered low, exemplified by a dehydrogenase activity below 10 μg TPF g^{-1} 16 h^{-1} (Figure 1A). This low microbiological activity in G and VF was stimulated by the amendments in the Technosols and the establishment of a pasture. The higher enzymatic activities in Technosols were indicative of the well-functioning microbial communities involved in organic matter degradation, mineralisation processes, and nutrient cycling [33], as the enzymes evaluated were implicated in nutrient cycling, such as C (β-glucosidase and cellulase), N (protease and urease), and P (acid phosphatase).

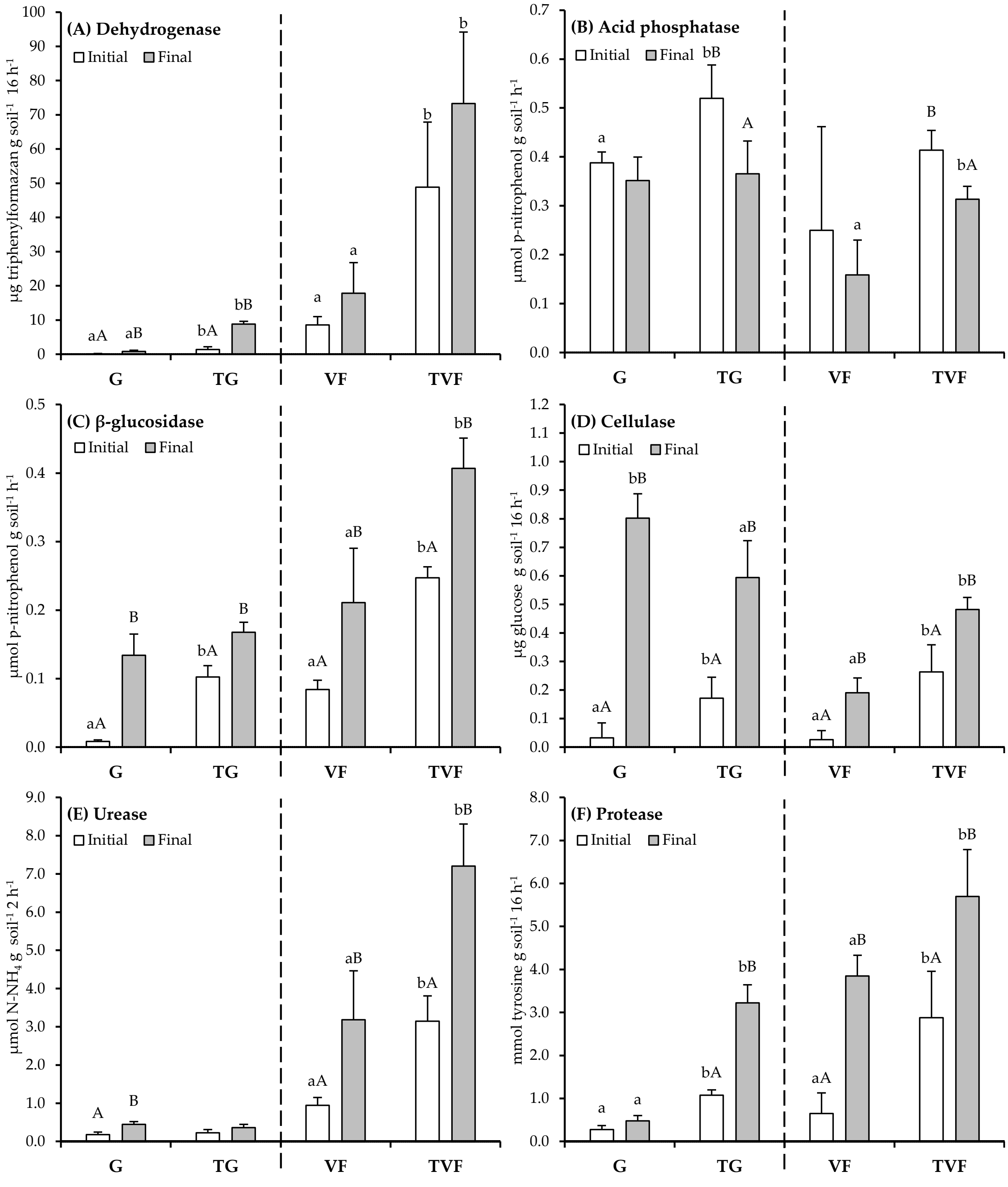

Figure 1. Enzymatic activities (dehydrogenase (**A**), β-glucosidase (**B**), acid phosphatase (**C**), cellulase (**D**), urease (**E**), and protease (**F**)) in the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF). Lower-case letters indicate significant differences between the control (G or VF) and the respective Technosol (TG or TVF) at each time; and capital letters indicate significant differences in each treatment with respect to time (beginning and end of pasture cultivation) (U test Mann–Whitney).

In gossan waste (G_i and G_f), the dehydrogenase activity was almost 0, and in Technosol/Gossan (TG_i), although it was also reduced/small, it increased by 15 times. With the development of pasture (TG_f), it increased by a further six-fold (Figure 1A). Similarly, although some dehydrogenase activity was already present in saline Fluvisol (FV_i), it was six times higher (~50 µg TPF g^{-1} 16 h^{-1}) in Technosol/Fluvisol (TVF_i) and with the pasture

(TVF_f) even higher (~75 µg TPF g^{-1} 16 h^{-1}), reaching values like those of healthy grassland soils, agricultural soils, and Mediterranean forest soils [45].

Both enzymatic activities related to the C-cycle were also enhanced significantly by both Technosols and pasture (Figure 1C,D). The β-glucosidase activity in TG_i was 10 times higher than in G_i. Moreover, with the development of pasture, it increased in TG_f and especially in G_f. A similar trend was observed for cellulase, but with a sharper increase caused by pasture growth. In VF, β-glucosidase activity was higher than cellulase activity at initial conditions and the same stimulation as in G with Technosols and pasture occurred, although it was stronger for β-glucosidase.

The pattern with the N-cycle-related enzymes was quite similar, although with much more evident changes in VF/TVF than in G/TG (Figure 1E,F). For example, in G and TG, urease activity was below 0.5 µmol N-NH_4 g^{-1} 2 h^{-1} in all cases; in TG, it did not increase with respect to G and, with pasture, it increased slightly and was only statistically significant in G. Yet, in TVF_i, urease activity tripled with respect to VF_i due to the increased concentration of N_T (Table 1), and, with pasture, it tripled in VF_f and doubled in TVF_f. As for protease, the behaviour in VF/TVF was similar to that of urease, while in G/TG there were marked changes, unlike urease. In G, there was a slight non-significant increase after pasture cultivation; moreover, in TG_i, the protease activity was about four times higher than in G_i and, with the pasture growth, it almost tripled in TG_f.

Unlike the other studied enzymatic activities, both G_i and VF_i showed acid phosphatase activity under initial conditions (0.39 and 0.25 µmol ρ-nitrophenol g^{-1} h^{-1}, respectively), although these values were lower than those in Technosols (in µmol ρ-nitrophenol g^{-1} h^{-1}; TG_i: 0.52, TVF_i: 0.41) (Figure 1B). It has been reported that the presence of PHEs can diminish phosphatase activity [77]; however, other studies suggest that the impact of PHEs on phosphatase activity is not very pronounced, as observed in G, demonstrating a certain degree of resilience to these perturbations [78,79]. The higher activity in Technosols can be attributed to the soil pH [55]. Unlike other enzymes, acid phosphatase activity decreased with pasture growth, possibly because legumes, which release more phosphatase enzymes than non-legumes [55], did not regrow after the first mowing (Figure 2).

Figure 2. Aspect of pasture plants after growth on the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF) before the first and second cut simulating livestock grazing.

3.3. Ecotoxicological Characterisations of Gossan Waste, Salt-Affected Fluvisol, and Technosols

All the improvements in physicochemical properties, nutrient content, bioavailability of PHEs, and microbiological activity with the construction of Technosols have allowed the establishment of a pasture that can be devoted to livestock grazing [80].

One month after sowing, the pasture biomass generated until then was mown to simulate livestock grazing. At this time (first cut), VF pots showed very low seed germination; hence, only very few plants were found (Figures 2 and 3). In contrast, in G, seed germination followed by plant growth was observed in all pots, with a predominance of gramineous (*L. multiflorum*) over leguminous plants (Figure 2). This pasture reached a mean stem length of 10 cm and a shoot biomass of 1.41 g DW (Figure 3A). In TG and TVF, pasture growth showed a remarkable improvement (Figure 2), with plants reaching more than 15 cm in stem length in both Technosols and higher shoot biomass with 3.8 g DW in TG and 2.59 g DW in TVF (Figure 3). Moreover, the pasture had a higher biodiversity in both Technosols compared with G and VF, with the presence of many leguminous plants of the genera *Trifolium* and *Medicago* and gramineous plants of the genus *Lolium* (e.g., *L. multiflorum*).

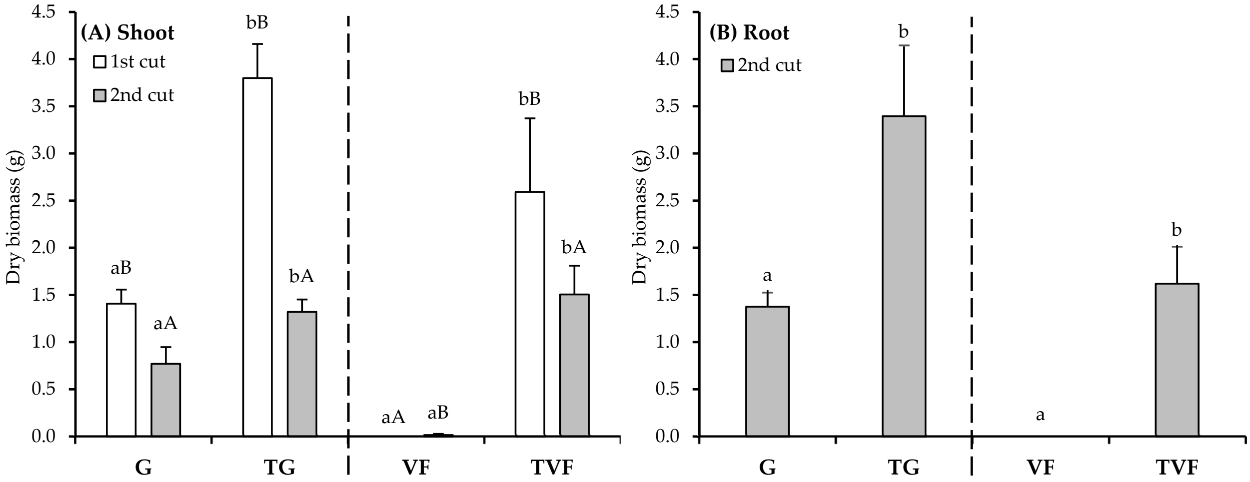

Figure 3. Development of pasture (dry biomass of shoot (**A**) and root (**B**)) grown in the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF). Lower-case letters indicate significant differences between the control (G or VF) and the respective Technosol (TG or TVF) at each time (1st and 2nd cut); and capital letters indicate significant differences in each treatment with respect to time (1st and 2nd cut) (U test Mann–Whitney).

Upon the first cut, the pasture was left to grow again for another month and then mown for the last time (second cut). During this time, *L. multiflorum* continued to grow to similar sizes as in the first mowing, while the leguminous plants did not regrow as effectively (Figure 2). A significant reduction in biomass production was observed in the second cut compared with the first cut, with values of 0.77 g DW in G, 1.32 g DW in TG, and 1.51 g DW in TVF (Figure 3A). As for the average root dry biomass, in TG it was twice as high as in G (3.40 vs. 1.38 g DW), and in TVF it was 1.62 g DW.

The concentrations of PHEs and nutrients in plant shoots in the pasture were measured to determine whether these plants can uptake them from the soil and translocate them to shoots. Thus, the potential of the ecotechnology based on the cultivation of pasture in Technosols for the remediation of marginal lands such as gossan waste and salt-affected soils with prospects for use as grazing areas was assessed. These considerations were particularly interesting in the case of G and TG, since, in TVF, the accumulation of PHEs was of no concern as they were in very low concentrations in the original soil [25] and consequently had low bioavailability (Table 3). In fact, most PHEs in plants grown in TVF were not present (i.e., As, Sb) or were at normal values in plants (i.e., Ni, Pb, Zn), except for Cu at concentrations below 50 mg kg^{-1} (Table 5), within the global toxic limit (normal: 5–30 mg kg^{-1}; toxic: 20–100 mg kg^{-1}) [68]. In general, plants grown in G accumulated higher concentrations of most PHEs (except Zn) than those grown in TG; conversely, in TG, pasture plants accumulated a higher amount of most nutrients (i.e., Ca, K, Mn, Mg, P) or similar amounts (i.e., Fe, Mo, Na, S) compared with G (Table 5).

Table 5. Total concentrations of potentially hazardous elements (PHEs) and nutrients in shoots of pasture plants grown in the gossan waste (G), salt-affected Fluvisol (VF), and Technosols from gossan (TG) and Fluvisol (TVF) (mean ± SD, $n = 4$).

Elements	**G**		**TG**		**VF**		**TVF**	
	1st Cut	**2nd Cut**	**1st Cut**	**2nd Cut**	**1st Cut**	**2nd Cut**	**1st Cut**	**2nd Cut**
As (mg kg^{-1})	62.55 ± 27.74 b	78.33 ± 26.22 b	16.07 ± 4.12 a	17.65 ± 3.92 a	-	-	bdl	bdl
Cu (mg kg^{-1})	25.12 ± 7.57 bA	57.09 ± 8.02 B	15.79 ± 2.55 aA	55.04 ± 1.32 B	-	-	46.74 ± 16.56	49.51 ± 6.31
Ni (mg kg^{-1})	10.63 ± 4.45 bB	6.20 ± 0.32 bA	4.15 ± 0.58 a	4.44 ± 0.39 a	-	-	5.00 ± 1.37	3.80 ± 0.67
Pb (mg kg^{-1})	160.39 ± 67.66 b	216.52 ± 71.06 b	27.99 ± 9.17 a	40.50 ± 10.90 a	-	-	0.98 ± 1.13	1.93 ± 2.23
Sb (mg kg^{-1})	2.78 ± 0.98	1.89 ± 1.52	bdl	bdl	-	-	bdl	bdl
Zn (mg kg^{-1})	46.75 ± 6.15 A	65.00 ± 4.39 aB	72.72 ± 27.08	85.82 ± 1.35 b	-	-	56.00 ± 7.59	59.37 ± 3.48
Ca (g kg^{-1})	5.95 ± 0.74 aB	4.43 ± 1.01 aA	14.43 ± 1.70 b	12.84 ± 0.94 b	-	-	3.59 ± 0.50	3.99 ± 0.72
Co (mg kg^{-1})	0.55 ± 0.22 b	0.48 ± 0.10	0.09 ± 0.18 a	bdl	-	-	bdl	bdl
Fe (g kg^{-1})	1.31 ± 0.46	1.25 ± 0.34 b	1.34 ± 1.86	0.49 ± 0.24 a	-	-	0.37 ± 0.41	0.50 ± 0.34
K (g kg^{-1})	15.29 ± 2.98 a	12.67 ± 2.08 a	26.51 ± 2.29 bB	21.47 ± 2.10 bA	-	-	33.29 ± 2.94 B	24.97 ± 4.76 A
Mn (mg kg^{-1})	57.29 ± 4.96 a	58.78 ± 14.24 a	100.48 ± 22.03 bA	207.89 ± 77.50 bB	-	-	25.50 ± 5.15	35.97 ± 5.83
Mg (g kg^{-1})	1.95 ± 0.13 aB	1.48 ± 0.38 aA	3.65 ± 0.52 b	3.47 ± 0.23 a	-	-	3.06 ± 0.21	3.20 ± 0.28
Mo (mg kg^{-1})	4.56 ± 6.56	bdl	3.30 ± 1.43 A	6.66 ± 1.38 B	-	-	3.54 ± 0.79	3.31 ± 0.11
Na (g kg^{-1})	6.16 ± 1.03 A	9.78 ± 0.48 B	9.19 ± 3.62	7.31 ± 2.84	-	-	26.86 ± 2.91	24.54 ± 3.44
P (g kg^{-1})	3.12 ± 0.47 a	2.74 ± 0.14 a	5.29 ± 0.64 b	5.76 ± 0.17 b	-	-	6.76 ± 0.83	7.26 ± 0.55
S (g kg^{-1})	9.61 ± 1.34 b	8.26 ± 1.03	7.90 ± 0.95 a	8.29 ± 2.16	-	-	3.39 ± 0.05	3.76 ± 0.56

SD—standard deviation, bdl—below detection limit. Lower-case letters indicate significant differences between the control (G or VF) and the respective Technosol (TG or TVF) at each time (1st and 2nd cut); and capital letters indicate significant differences in each substrate with respect to time (1st and 2nd cut) (U test Mann–Whitney).

The concentration of Fe in plant shoots grown in G and TG was significantly above typical values in plants (50–250 mg kg^{-1} [81]), and Ca and Mg were at levels within the normal range in both G and TG (Ca: 2–40 g kg^{-1}; Mg: 1–8 g kg^{-1} [81]); however, K was in deficit concentrations (<20–25 g kg^{-1} [81]). Zinc, which has a micronutrient–PHE duality depending on the concentration, was in the optimal range for good plant development (Zn: 25–150 mg kg^{-1} [81]) in plants grown in G and TG, while Cu, with the same behaviour, was found in concentrations slightly above the optimal range in the first cut in both G and TG (Cu: 5–20 mg kg^{-1} [81], 5–30 mg kg^{-1} [68]) and in the second cut was within the toxic limit (20–100 mg kg^{-1} [68]). The accumulated As and Pb in G (As: 62–78 mg kg^{-1}; Pb: 160–216 mg kg^{-1}) were much higher than in TG (As: 16–18 mg kg^{-1}; Pb: 28–41 mg kg^{-1}); however, they remained in TG within the lower limits (considered excessive or phytotoxic (As: 5–20 mg kg^{-1}; Pb: 30–300 mg kg^{-1} [68])).

Moreover, to test whether this strategy of converting degraded areas into grazing areas by combining Technosols and pasture growth was valid, it was necessary to assess the safety of the consumption of these plants by animals. For this purpose, the concentrations of PHEs in shoots were compared with the maximum tolerable levels of PHEs in feed for typical grazing species (cattle and sheep) (in mg kg^{-1}; As: 30, Cu: 40—cattle, 15—sheep, Ni: 100, Pb: 100, Zn: 500—cattle, 300—sheep [80]). In this sense, the plants grown in G exceeded the regulatory limits of As, Cu, and Pb, and, in the pasture grown in TG and TVF, they only exceeded the regulatory limit of Cu. Thus, although these results are encouraging, food safety cannot be assured and future studies may consider the design of Technosols with a higher proportion of waste to reduce plant uptake of this PHE. Furthermore, the use of pasture biomass generated as a source of energy production [82] could also be explored, given that the problem of the accumulation of PHEs such as Cu would not be as critical for this purpose.

4. Conclusions

Both the gossan waste from the São Domingos mine and the salt-affected Fluvisol from the Sobralinho salt marsh area constitute degraded environments that require restoration actions. To this end, the integrated green biotechnology approach based on the construction of Technosols from these degraded materials together with a combination of organic/inorganic wastes from local industries (urban gardening services, quarries, cafes, and breweries), followed by the development of pasture, has demonstrated an enormous potential to improve their unfavourable conditions in the timespan tested (2 months) under greenhouse conditions.

Technosols not only mitigate the main disturbances (acidity and PHE bioavailability in gossan waste; salinity and sodicity in Fluvisol), but also improve their microbiological activity, fertility, and structure, which prevent the development of healthy vegetation. This, in turn, allows the cultivation of a biodiverse pasture, including glycophytic plants such as legumes (*Trifolium* sp. and *Medicago* sp.) and grasses (*Lolium* sp.). The pasture in both Technosols grew vigorously, with no visible signs of toxicity, while in the Fluvisol it hardly grew at all and in the gossan waste it grew less and accumulated more PHEs in the shoots. Indeed, plants grown on the gossan waste accumulated As, Cu, and Pb in concentrations unsuitable for use in feed for typical grazing species (cattle and sheep), whereas only the regulatory limit for Cu was exceeded in the pasture plants grown in TG and TVF.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Table A1. Pseudo-total concentrations of potentially hazardous elements (PHE) in mg kg^{-1} present in the gossan waste (G) and salt-affected Fluvisol (VF) (mean ± SD, *n* = 4).

Elements (mg kg^{-1})	G	VF
As	9126.67 ± 238.77	15.6 ± 0.01
Cd	0.11 ± 0.08	0.08 ± 0.01
Cu	218.67 ± 5.81	27.33 ± 0.69
Hg	26.67 ± 6.67	0.07 ± 0.01
Mn	27.67 ± 1.76	598.32 ± 12.27
Ni	2.77 ± 0.43	27.50 ± 0.67
Pb	29,633.33 ± 554.78	37.73 ± 2.19
Zn	83.33 ± 6.62	103.67 ± 1.89

SD—standard deviation. Values of G are extracted from [58] and of VF from [25].

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