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Unveiling a Technosol-based remediation approach for enhancing plant growth in an iron-rich acidic mine soil from the Rio Tinto Mars analog site

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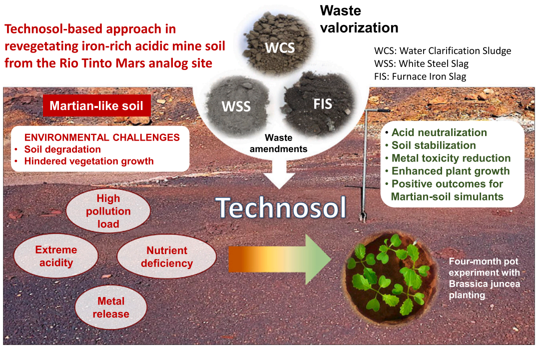
HIGHLIGHTS

- Circular economy for sustainable Technosol-based soil remediation
- Soil stabilization and plant growth in extreme environments is challenging but achievable.
- Reduction of soil acidity and metal mobility to environmentally sustainable levels
- Promising results for future applications in Martian soil simulants

GRAPHICAL ABSTRACT



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ABSTRACT

This paper explores the potential of Technosols made from non-hazardous industrial wastes as a sustainable solution for highly acidic iron-rich soils at the Rio Tinto mining site (Spain), a terrestrial Mars analog. These mine soils exhibit extreme acidity ($pH_{H2O} = 2.1–3.0$), low nutrient availability (non-acid cation saturation < 20 %), and high levels of Pb (3420 mg kg^{-1}), Cu (504 mg kg^{-1}), Zn (415 mg kg^{-1}), and As (319 mg kg^{-1}), hindering plant growth and ecosystem restoration. To address these challenges, the study systematically analyzed selected waste materials, formulated them into Technosols, and conducted a four-month pot trial to evaluate the growth of *Brassica juncea* under greenhouse conditions. Technosols were tailored by adding varying weight percentages of waste amendments into the mine Technosol, specifically 10 %, 25 %, and 50 %. The waste amendments comprised a blend of organic waste (water clarification sludge, WCS) and inorganic wastes (white steel slag, WSS; and furnace iron slag, FIS). The formulations included: (T0) exclusively mine Technosol (control); (T1) 60 % WCS + 40 % WSS; (T2) 60 % WCS + 40 % FIS; and (T3) 50 % WCS + 16.66 % WSS + 33.33 % FIS. The analyses covered leachate quality, soil pore water chemistry, and plant response (germination and survival rates, plant height, and leaf number). Results revealed a significant reduction in leachable contaminant concentrations, with Pb (26.16 mg kg^{-1}), Zn (4.94 mg kg^{-1}), and Cu (2.29 mg kg^{-1}) dropping to negligible levels and shifting

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towards less toxic species. These changes improved soil conditions, promoting seed germination and seedling growth. Among the formulations tested, Technosol T1 showed promise in overcoming mine soil limitations, enhancing plant adaptation, buffering against acidification, and stabilizing contaminants through precipitation and adsorption mechanisms. The paper stresses the importance of tailoring waste amendments to specific soil conditions, and highlights the broader implications of the Technosol approach, such as waste valorization, soil stabilization, and insights for *Brassica juncea* growth in extreme environments, including Martian soil simulants.

1. Introduction

The exploration of Martian surface and its potential for supporting plant growth is an active area of research in Astrobiology (Eichler et al., 2021; Medina et al., 2021). The challenges posed by Martian soil for sustaining plant life under terrestrial conditions such as nutrient scarcity and potential toxicity requires substantial modifications. This involves creating an environment suitable for plant survival and growth, including the addition of organic matter, nutrients, water, and pH adjustments. Studies have shown that certain plant species can germinate and grow in Mars soil simulants under optimal conditions (Silverstone et al., 2005; Wamelink et al., 2014; Kasiviswanathan et al., 2022; Caporale et al., 2023). However, these simulants may not accurately replicate actual Martian soil, and there are uncertainties about the extent to which they can support plant growth.

An alternative approach to explore the potential of Martian soil is to investigate analogous extreme environments on Earth (Marlow et al., 2008; Preston and Dartnell, 2014). These terrestrial analog sites provide valuable insights into physical, geochemical, and microbiological processes that might have taken place on the red planet (Navarro-González et al., 2003; Peters et al., 2008; Valdivia-Silva et al., 2016). They can also serve as a testing ground for Mars exploration instruments, and aid in interpreting the formation mechanisms of iron oxide-rich soils (Marlow et al., 2008).

The Rio Tinto mine site (Fig. 1), in southwestern Spain, is recognized as a terrestrial analog site of significant interest for studying the Terra Meridiani hematite region of Mars due to mineralogical and geochemical similarities (Fernández-Remolar et al., 2004; Amils et al., 2007, 2014; Edwards et al., 2007; Sánchez-García et al., 2020). The NASA's Mars Exploration Rovers have detected the presence of hematite, jarosite, and evaporitic sulfate minerals (Klingelhöfer et al., 2004; Chevrier and Mathé, 2007; Edwards et al., 2007; Hazen et al., 2023) providing in situ evidence for an ancient aqueous environment at Meridiani Planum (Squyres et al., 2004). In terrestrial environments, the inferred mineral assemblage is often linked to near-surface processes involving the oxidative dissolution of pyrite and the subsequent acid-sulfate chemical reactions that drive under highly acidic and oxidizing conditions, similar to the environment found at the Rio Tinto analog site (Fernández-Remolar et al., 2005).

Historically, the Rio Tinto mining district engaged in extensive open-air sulfide roasting operations to extract copper from low-grade ores (Salkield, 1987). The roasted mineral was subjected to acid leaching with mine water leaving a solid residue of ferric iron oxide (red waste) on the calcination grounds (Fig. 1a). Meanwhile, the leach liquors were transferred into cementation tanks where dissolved copper was precipitated by using iron scrap chips. Interestingly, the iron-rich contaminated soil resulting from this ancient metallurgical process (Fig. 1b) shares similarities with hematite-rich Martian regions in terms of its chemical and mineralogical composition. Nutrient deficiencies coupled with extreme acidity, and elevated levels of sulfate and phytotoxic trace elements create an inhospitable environment for plant growing in this mine Technosol (Fernández-Landero et al., 2023).

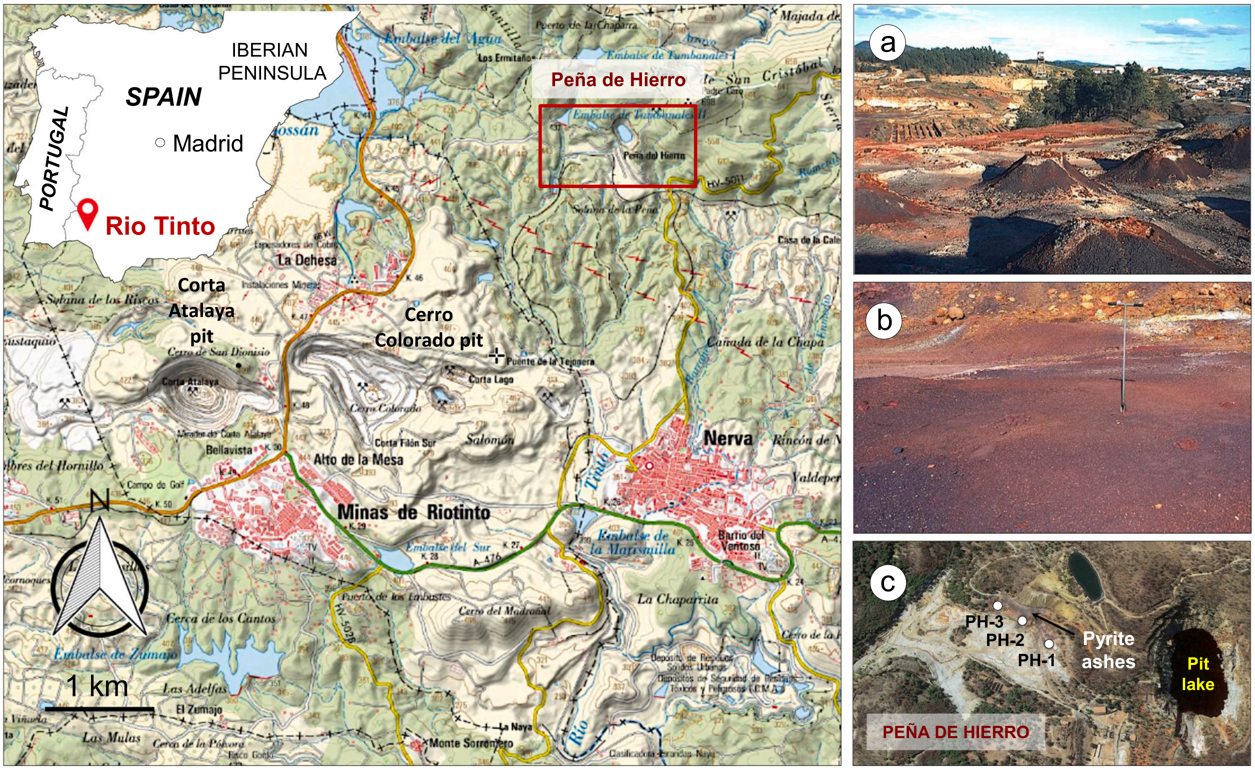

Fig. 1. Map of the Rio Tinto mining area (viewfinder SIGPAC) and illustrative images showing (a) roasted pyrite heaps; (b) mine Technosol contaminated with roasted pyrite wastes; and (c) sampling locations at the Peña de Hierro mine site.

Moreover, prolonged exposure to pollutants could lead to chronic health issues for human and wildlife populations. As such, effective management of this environmentally significant soil requires the adoption of sustainable remediation strategies to minimize the dispersion of contaminants and their potential associated risks. The application of Technosol-based methods for in situ immobilization of contaminant trace elements may offer a cost-effective and eco-friendly approach to land reclamation (Séré et al., 2008; Novo et al., 2013; Watkinson et al., 2017; Forján et al., 2018; Santos et al., 2019; Weiler et al., 2020; Ruiz et al., 2023). This remediation strategy involves the use of soil amendments derived from non-hazardous waste materials to create a conducive environment for the establishment of plants. The combined use of waste amendments and revegetation in mine soils offers several advantages (Tordoff et al., 2000; Fernández-Caliani et al., 2021), including: (i) immobilization of contaminants in the rhizosphere; (ii) reduction of risk exposure to wind-blown or re-entrained toxic particulates through ingestion or inhalation; (iii) aesthetically pleasing and publicly accepted landscape; (iv) beneficial habitat for wildlife.

By adopting a circular economy approach, this study addresses challenges linked to plant growth within a Martian-like mine soil, offering insights for optimizing soil properties and plant development. Specifically, it was aimed to assess the effectiveness of chemical stabilization in alleviating soil acidity and reducing the availability of toxic elements for plants. Additionally, it seeks to analyze the adaptability and resilience of *Brassica juncea* (L.) Czern, a known metal-tolerant plant, under tailored waste amendment combinations, focusing on germination and seedling growth patterns.

2. Materials and methods

2.1. The mine Technosol

The study area, located at the Peña de Hierro site in the Rio Tinto mining district (Fig. 1c), features a unique mine soil characterized by significant amounts of technogenic artifacts (red waste) resulting from past pyrite roasting processes. This residue poses a challenge to vegetation establishment, hindering the application of phytoremediation techniques. Classified as a Spolic Toxic Technosol according to World Reference Base for Soil Resources (Schad, 2018), the mine soil is composed mainly of well-crystallized hematite, lending it a distinct reddish hue (dry soil color Munsell chart 10R 4/2) reminiscent of the iron oxide prevalent on the Martian surface (Chevrier and Mathé, 2007). It also includes jarosite, quartz, amorphous or poorly ordered Fe phases, and minor constituents such as mica, kaolinite, feldspars, barite, anglesite, and efflorescent salts of iron sulfates (Fernández-Landero et al., 2023). Unlike relatively insoluble sulfate minerals (barite, anglesite, jarosite), the efflorescent salts undergo cycles of dissolution and reprecipitation due to dynamic wetting and drying conditions.

Soil analysis (Table 1) of the top layer (0–20 cm), extracted with an Edelman hand auger and previously analyzed by Fernández-Landero et al. (2023), revealed silt loam texture, extremely acidic soil reaction (pH_{H2O} = 2.1–3.0), strongly oxidizing conditions (Eh = 751 ± 46 mV), and relatively low electrical conductivity (< 1.8 mS cm^{-1}). Upon exposure to hydrogen peroxide, pH_{H2O2} values fall within the range of pH_{H2O} values, indicating a scarcity of sulfide minerals. Pyritic sulfur content was relatively low (0.15–0.18 %), confirming minimal unroasted sulfide ores in the red waste. Notably, sulfate was the predominant sulfur form (0.78–1.71 %), mainly due to jarosite-group minerals, resulting in an estimated modest release of latent acidity from sulfide oxidation (approx. 100 mmol H^+ per kg of soil or 3.06 kg of H_2SO_4 per ton). Importantly, results from an H_2O_2-based static test (Fernández-Landero et al., 2023) revealed that potential acid-consuming phases were ineffective in neutralizing sulfidic acidity, as evidenced by the mean value of net acid generation (NAG = 114 mmol H^+ kg^{-1}). Nutrient deficiencies are evident with low total carbon content (0.07 %) and reduced levels of exchangeable non-acid cations (mean non-acid cation saturation of 12 %), reflecting the limited nutrient-supplying capacity of the highly acidic mine soil.

Table 1
Soil properties and total concentrations of major and trace elements determined by ICP-OES on the <2 mm size fraction.

Parameter	Mine soil samples				
	PH-1	PH-2	PH-3	Mean	Std. Dev.
Sand (%)	15.9	15.0	18.0	16.3	1.5
Silt (%)	69.0	74.3	71.0	71.4	2.6
Clay (%)	15.1	10.7	11.1	12.3	2.4
Electrical conductivity (mS cm^{-1})	1.66	1.49	1.78	1.64	0.15
Eh (mV)	698	786	768	751	46
pH_{H2O}	3.0	2.5	2.1	2.5	0.4
pH_{H2O2}	2.8	2.5	2.4	2.6	0.2
Net acid generation (mmolH^+/kg)	144	104	93.3	114	26.9
$S_{sulfate}$ (g kg^{-1})	17.1	7.8	10.7	11.9	4.8
S_{pyrite} (g kg^{-1})	1.8	1.5	1.6	1.6	0.2
C_{total} (g kg^{-1})	0.8	0.5	0.7	0.7	0.2
Cation exchange capacity ($cmol^+kg^{-1}$)	14.2	2.5	4.0	6.9	6.3
Base saturation (%)	5.6	18.7	11.7	12.0	6.5
Major elements (g kg^{-1})					
Al	22.6	3.0	4.6	10.1	10.9
Ca	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	352	461	470	428	65.7
K	7.1	1.3	1.9	3.4	3.2
Mg	0.4	0.1	0.1	0.2	0.2
Na	1.4	0.3	0.8	0.8	0.6
Trace elements (mg kg^{-1})					
As	319	150	152	207	97
Bi	86	108	100	98	11
Cd	3	3.3	3.1	3.1	0.2
Co	46	46	47	46	0.6
Cr	18	7	9	11	5.9
Cu	504	400	384	429	65
Ni	8	8	9	8	0.6
Pb	2340	3420	2980	2913	543
Tl	12	17	15	15	3
Zn	415	314	311	347	59

Given the dominance of iron-rich minerals, particularly hematite, iron was the most abundant major element in the mine soil samples, with an average content of 42.8 wt%. Other major elements such as Al, Mg, Ca, Na, and K were present at concentrations generally below 1 wt %. Total concentrations of potentially hazardous elements consistently remained at elevated levels, with Pb (up to 3420 mg kg^{-1}), Cu (up to 504 mg kg^{-1}), Zn (up to 415 mg kg^{-1}), and As (up to 319 mg kg^{-1}) being the major contributors to the trace element budget. Moreover, the mean contents of Bi, Co, Tl, and Cd peaked at 98 mg kg^{-1}, 46 mg kg^{-1}, 15 mg kg^{-1}, and 3.1 mg kg^{-1}, respectively. Trace element concentrations surpassed regional geochemical background by one to two orders of magnitude (Galán et al., 2008), collectively pointing to an extremely high degree of multi-elemental contamination (Romero et al., 2006; Fernández-Landero et al., 2023; Yesares et al., 2023). Concentrations of Pb, As, and Tl exceeded screening levels for evaluating contaminated soils in Southern Spain (Junta de Andalucía, 2015), posing unacceptable risks to potential receptors. Consequently, effective measures are imperative to mitigate potential exposure to soil contaminants.

2.2. Experimental setup

The experimental setup encompassed several key steps, including the selection and characterization of non-hazardous waste materials, formulation and blending process, physical and chemical testing, and trials with plants in pots. All these steps were designed to ensure the development of Technosols capable of enhancing soil quality for vegetation restoration.

2.2.1. Selection of waste materials for Technosol-based remediation

Three industrial wastes were selected as secondary raw materials for constructing Technosols: (i) sludge generated during the process of water clarification (WCS); (ii) white slag from steel making industry (WSS); and (iii) furnace slag from iron production (FIS). These waste materials, classified as non-hazardous under the codes 19 09 02, 10 02 02, and 10 09 03, respectively, within the European Waste Catalogue (Commission Decision 2000/532/EC), are abundantly generated and readily available on a global scale. Annually, drinking water treatment plants produce millions of tons (Mt) of sludge, with the volume steadily increasing due to the growing demand for water (Nguyen et al., 2022). In 2022, the global production of blast furnace slags ranged from 330 to 390 Mt., while steel-making slags amounted to between 190 and 290 Mt. (USGS, 2023). WCS sludge typically contains solid particles, organic matter, and other substances that have been removed by coagulation and flocculation processes during drinking water treatment. This residual material was incorporated as an organic component into the Technosol, enhancing soil structure and water retention capacity, while also providing essential macronutrients (N, P, K, S, and Mg) for improved soil fertility (Dassanayake et al., 2015; Watkinson et al., 2017). WSS and FIS slags have potential as liming agents, for assisting acid-neutralization and removal of trace elements and Fe(II) from acid mine drainage systems (Yang et al., 2022). Currently, these materials have no further utility and are being consistently disposed of in a landfill located at Nerva, within the Rio Tinto mining area. The company managing the landfill provided representative samples of the waste materials specifically for this study.

Before constructing Technosols, a comprehensive characterization of the chosen waste materials was performed, analyzing physical and chemical properties to ensure their suitability for chemical stabilization and potential adverse effects on soil quality and plant growth. The waste samples were air-dried, gently disaggregated, and sieved to 2 mm. Analysis covered particle size distribution, pH (in water), Eh, electrical conductivity, carbon contents (total, organic, and inorganic), nutrient contents (total nitrogen, assimilable phosphorus and potassium), mineral composition, and total concentrations of major elements (Fe, Al, Mg, Ca, Na, K, P, Ti, S) and trace elements of environmental significance (As, Bi, Cd, Co, Cr, Cu, Hg, Ni, Pb, Tl, Zn). In addition, a leaching test was conducted following European Standard EN-12457-4, using a liquid-to-solid ratio of 10 L kg^{-1} with end-over-end agitation for 24 h. This aimed to quantify potentially toxic trace elements that could leach from the waste material when exposed to rainfall. The leachate solutions were filtered through 0.45 μm syringe filters, acidified with dilute nitric acid, and stored in polyethylene bottles at 4 °C until analysis.

2.2.2. Constructed soil formulation

The Technosol-based remediation strategy involved the formulation of engineered soils tailored for remediating mining areas contaminated with red wastes. Waste amendments were prepared by manually blending WCS, WSS, and FIS in predetermined ratios to achieve a balanced combination of organic and inorganic components, allowing for enhanced fertility and contaminant immobilization capability. The chosen formulation ratio was 60:40 (*w*/w), meaning 60 % organic waste and 40 % inorganic waste on a dry weight basis. An exception was made for one Technosol, which tested an equal proportion of organic (50 % WCS) and inorganic (16.66 % WSS and 33.33 % FIS) waste materials. Similar ratios are usually reported in the literature for the formulation of tailor-made Technosols from wastes for the restoration of degraded mining areas (e.g. Yao et al., 2009a, 2009b; Santos et al., 2016; Asensio et al., 2019).

The Technosols were created through a blending process, where the waste material mixture, referred to as waste amendments, was thoroughly hand-mixed with the most representative sample of the mine soil (PH-2). To tailor the Technosols to the unique characteristics of the red mine soil, adjustments were made to the amendment mixtures. Thus, distinct Technosols were crafted by adding varying weight percentages of waste amendments into the mine soil, specifically 10 %, 25 %, and 50 %, in order to test the effect of the waste content on Technosol performance. The mine soil sample PH-2 was selected as the control for the laboratory experiment, providing a baseline measurement to assess the influence of the amendments on soil properties. Overall, there were eight mixtures (T0, T1a, T1b, T1c, T2a, T2b, T2c, and T3) including the control (Table 2).

Additionally, both untreated soil and soil treated with waste amendments were subjected to the EN-12457-4 leaching test to evaluate leachability and the quality of the resulting leachates. This evaluation played a crucial role in selecting optimal blends for growing purposes. The chosen blends were manually homogenized thoroughly and then moistened with distilled water to water-holding capacity (24–34 % dry weight). Subsequently, they were placed in polypropylene containers and left at room temperature (20 ± 4 °C) for two weeks to allow for equilibration before being transferred to pots.

2.2.3. Pot experiment with Brassica juncea growth

In the next phase of the experimental setup, a pot trial was carried out with Indian mustard (*Brassica juncea*, var. scala) to assess the effects of waste amendments on plant establishment and development. *B. juncea* is a versatile herbaceous plant native to the Indian subcontinent, cultivated globally due to its adaptability to diverse climatic conditions and various soil types. The selection of this species was based on its rapid growth rate and dense root system, which significantly contributes to enhanced soil fertility and stability. Given its remarkable tolerance to potentially toxic trace elements, *B. juncea* is suitable for phytostabilization and revegetating mine soils (Novo and González, 2014; Pérez-Esteban et al., 2014; Forján et al., 2018). It also serves as a valuable indicator of phytoavailability, assessing the effectiveness of potential remediation treatments in metal-contaminated soils (Clemente et al., 2005). High-quality seeds were supplied by AgroEcology (El Ejido, Almería, Spain) and carefully selected to ensure uniformity and viability.

Potting mixtures, each weighing approximately 3.5 kg, were prepared by mixing predetermined ratios of mine soil and waste amendments, and filled into individual pots of appropriate size (15 cm depth and 15 cm diameter) with tiny drainage holes at the base to prevent

Table 2
Formulation of the Technosols produced from water clarification sludge (WCS), white steel slag (WSS), and furnace iron slag (FIS), with the mixing percentage expressed in weight percent.

Sample	Technosol	Technosol composition		Amendment composition		
PH-2	Control	100 % mine soil	0 % amendment	–	–	–
T1a	S2T8–10	90 % mine soil	10 % amendment	60 % WCS	40 % WSS	-
T1b	S2T8–25	75 % mine soil	25 % amendment	60 % WCS	40 % WSS	–
T1c	S2T8–50	50 % mine soil	50 % amendment	60 % WCS	40 % WSS	–
T2a	S2T11–10	90 % mine soil	10 % amendment	60 % WCS	–	40 % FIS
T2b	S2T11–25	75 % mine soil	25 % amendment	60 % WCS	–	40 % FIS
T2c	S2T11–50	50 % mine soil	50 % amendment	60 % WCS	–	40 % FIS
T3	S2T13–25	75 % mine soil	25 % amendment	50 % WCS	16.66 % WSS	33.33 % FIS

WCS: Water Clarification Sludge. WSS: White Steel Slag. FIS: Furnace Iron Slag.

waterlogging. A layer of gravel was placed beneath of each pot to prevent soil leakage. Before planting, germination testing was conducted on *B. juncea* seeds to assess seed viability and evaluate the suitability of the constructed Technosols for promoting seedling establishment. For each Technosol, the seeds were spread on Petri dishes (30 seeds per plate), moistened with tap water, and subjected to day (10 h)-night (14 h) light cycles at temperatures ranging from 18 to 22 °C. Germination progress was observed and recorded over a period of 4–6 days. Following successful germination, five *B. juncea* seedlings, having reached the stage with two fully expanded cotyledons, were carefully transferred to the pots filled with Technosol, allowing enough space for plant growth. For quality control and accurate testing, three replicate pots of each Technosol were prepared. Additionally, a single pot was exclusively filled with mine soil (sample PH-2), without any sown seeds, while another pot was filled with mulch and used for planting, serving as the control treatment.

The pots were placed inside a glasshouse environment under natural sunlight conditions. Over the experimental period, extending from February to May 2023, temperatures ranged from 10 °C to 42 °C, air humidity levels varied between 25 % and 80 %, and daily light exposure lasted 10.5 to 14.5 h. The pots were regularly irrigated with tap water ($pH = 6.85$; $EC = 0.65\ mS\ cm^{-1}$) to maintain optimal moisture levels for plant growth, avoiding overwatering or waterlogging. The moisture levels typically ranged from 65 % to 75 % of the soil water-holding capacity. Tap water was administered three times a week at a rate of either 50 mL or 100 mL, depending on the evaporation rate. Throughout the experiment, relevant parameters including pH, electrical conductivity and chemical composition of soil pore water, were regularly measured and recorded for both Technosols and the control sample. These measurements were conducted monthly for four months.

Soil solution sampling was performed under moisture conditions equivalent to field capacity using Rhizon soil moisture samplers (Eijkelkamp, The Netherlands) inserted into the soil at a 45° angle. This consists of a porous polymer tube with a pore size of 0.15 μm connected to a PVC tube and a Luer-Lock connector (Clemente et al., 2008). Soil pore water was sampled by pulling a vacuum with a 50 mL syringe and used immediately for pH, Eh, and electrical conductivity measurements. The extracted solution was then acidified with dilute nitric acid for the subsequent analysis of element concentrations in the soluble fraction. Furthermore, survival rate and parameters such as plant height and leaf number were measured to monitor the growth and development of *B. juncea*. These measurements were consistently recorded at regular intervals, weekly over a span of four months.

2.3. Analytical methods

The analysis of grain-size distribution and specific surface area was conducted using the Mastersizer 3000 laser diffraction particle size analyzer. The pH, redox potential (Eh), and electrical conductivity of the samples were determined through potentiometric measurements in the supernatant suspension obtained by mixing 10 g of soil with 25 mL of deionized water, followed by stirring for 5 min and allowing it to stand for 30 min.

Total carbon (C_{total}) and total nitrogen contents were determined using an ELTRA CHS-580 A analyzer through a dry combustion method. Inorganic carbon (C_{inorg}) measurement involved a two-step process: initially, the samples were calcined in a muffle furnace set at 400 °C for 16 h. Prior to this, a dehydration step was performed, wherein the samples were subjected to 110 °C heat for 1 h to remove moisture. Organic carbon (C_{org}) quantification was derived as the difference between C_{total} and C_{inorg} (Nelson and Sommers, 1996). To convert organic carbon to organic matter, a conversion factor of 1.724 was applied. Plant-available phosphorus concentration was assessed using Olsen's method, which relies on alkaline phosphate extraction with a 0.5 N NaH (CO_3) solution (Olsen and Sommers, 1982), while the content of assimilable forms of potassium was determined through a 0.01 M $CaCl_2$ extract (Houba et al., 1996).

Chemical analysis of total concentrations of major and trace element was performed by ICP-OES after a four-acid ($HClO_4$-HNO_3-HCl-HF) digestion process at Actlabs (Ancaster, Ontario, Canada), an accredited laboratory compliant with ISO 9001 and ISO/IEC 17025 standards. Quality control measures, including the use of reagent blanks, duplicate analysis, and certified reference materials (OREAS 101b, OREAS 98, and OREAS 13b), were employed to ensure accuracy and precision. The analysis of reference materials indicated deviations from certified concentrations with a relative standard deviation (RSD) of <10 %, and the precision of analytical data consistently was better than 5 % RSD for all reported elements.

Element concentrations in both the leachate solution and soil pore water extracted with Rhizon samplers were subjected to chemical analysis. Major elements were measured using an Agilent 5110 ICP-OES, while trace elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent 7700 instrument. For quality control, external calibration, internal standard, replicates, blank analysis and standard reference material (SRM 1640a) were used. All elements in the standard reference material fell within the range of 95 % and 106 % of the certified concentrations. Analytical data for the majority of studied elements displayed accuracy and precision with an RSD better than 10 %. Furthermore, soil solution analysis for chloride, fluoride, and nitrate anions was conducted using ion chromatography with a Metrohm 883 Basic IC plus instrument. Mineral saturation indices and distribution of aqueous species in the soil solution were computed using the geochemical modeling software PHREEQC (Parkhurst and Appelo, 2013) and the Minteq.v4 thermodynamic database (Allison et al., 1999), enlarged with data from Bigham et al. (1996) to account for schwertmannite. The saturation index (SI) for each predicted mineral was calculated using the formula:

$$SI = log\ (IAP/Ks)$$

where IAP is the ion activity product and K_s is the solubility product constant. This index provides insights into potential dissolution-precipitation reactions, thereby influencing the availability of toxic elements to plants. A SI approaching zero indicates solubility equilibrium in the pore water composition. A positive SI implies potential oversaturation and precipitation, while a negative value indicates undersaturation, suggesting potential dissolution.

Additionally, a mineralogical analysis was carried out by powder X-ray diffraction (XRD) on a BRUKER D8-Advance diffractometer, using monochromatic CuKα radiation at 40 kV and 30 mA. XRD patterns were obtained from randomly oriented powders scanned from 3° to 70° 2θ, with a step size of 0.02° and a counting time of 0.6 s per step. Soil minerals were visualized by high-resolution field emission scanning electron microscopy (FESEM) using a JEOL JSM-IT500HR instrument operated at 20 kV, and chemically analyzed with an energy-dispersive X-ray (EDS) spectrometer coupled to the FESEM.

2.4. Statistical analysis

The collected data underwent statistical analysis to evaluate the effects of the treatment on the chemistry of the soil pore water. Left-censored data, representing values below the detection limit, were managed by assuming them as half of the detection limit. Standard errors were calculated to gauge the variability between replicates. Statistical differences between the sample means of the Technosols and the control soil (mine soil without treatment) were assessed using the Student's *t*-test and one-way analysis of variance (ANOVA). Before conducting the ANOVA analysis, the homogeneity of variance was examined through Levene's test. A significance level of $\alpha = 0.05$ (95 % confidence interval) was set for all statistical tests.

3. Results and discussion

3.1. *Characteristics of waste materials used as amendments*

To avert potential environmental issues stemming from the use of non-hazardous wastes in tailor-made Technosol formulation, a thorough understanding of the properties and constituents of these residual materials is crucial (Yao et al., 2009a). The waste materials used as components of the Technosols showed distinct compositions and characteristics in terms of particle size distribution, electrical conductivity, pH, carbon content, nitrogen content, and nutrient availability (Table 3).

Specifically, WCS showed a light olive brown hue (2.5Y 5/3), a slightly acid to neutral reaction ($pH_{H2O} = 6.7$), and the lowest electrical conductivity (0.69 mS cm^{-1}), indicating a limited presence of soluble salts. Remarkably, it displayed the highest total carbon content at 11.80 %, coupled with a substantial organic carbon content of 11.50 %. In addition, WCS boasted the largest organic matter content at 19.83 %, highlighting its rich organic composition. With the highest total nitrogen content at 2.12 %, WCS could serve as a nitrogenous organic fertilizer. The C/N ratio of 5.6 is indicative of a good balance between carbon and nitrogen. Further enhancing its profile, WCS contained 16.7 mg kg^{-1} of available phosphorus and 57.7 mg kg^{-1} of available potassium, thus providing a source of essential nutrients for plant growth.

Table 3

Properties and chemical composition of the waste materials and their leachates.

Parameter	WCS	WSS	FIS
Specific surface area (m^2 g^{-1})	0.598	0.640	0.474
Electrical conductivity (mS cm^{-1})	0.69 ± 0.07	7.27 ± 0.06	0.78 ± 0.04
$pH_{(H2O)}$	6.74 ± 0.21	12.44 ± 0.11	10.00 ± 0.13
C_{total} (g kg^{-1})	118.0	15.0	17.0
$C_{inorganic}$(g kg^{-1})	3.0	15.0	7.0
$C_{organic}$(g kg^{-1})	115.0	n.d.	10.0
Organic matter (g kg^{-1})	198.3	n.d.	17.2
N_{total} (g kg^{-1})	21.2	0.1	0.9
$P_{available}$ (mg kg^{-1})	16.7	22.8	18.7
$K_{available}$ (mg kg^{-1})	57.7	151	56.0
Major elements (g kg^{-1}) — Solid waste			
Al	> 100	37.9	9.7
Ca	1.8	> 100	16.8
Fe	13.4	9.3	75.6
K	6.0	0.2	0.9
Mg	1.6	66.7	8.3
Na	0.6	0.9	2.9
P	1.75	0.01	0.24
S	7.8	4.2	0.4
Ti	< 0.1	1.2	0.3
Trace elements (mg kg^{-1}) — Solid waste			
As	42	< 2	26
Bi	< 2	< 2	< 2
Cd	< 0.5	< 0.5	< 0.5
Co	3	1	5
Cr	14	121	73
Cu	84	42	294
Hg	2	< 1	< 1
Ni	15	12	54
Pb	23	16	88
Tl	< 2	< 2	< 2
Zn	71	252	226
Trace elements (mg L^{-1}) — Leachate			
As	< 0.1	< 0.1	< 0.1
Cd	< 0.05	< 0.05	< 0.05
Cr	< 0.5	< 0.5	< 0.5
Cu	< 0.1	< 0.1	< 0.1
Hg	< 0.01	< 0.01	< 0.01
Ni	< 0.5	< 0.5	< 0.5
Pb	< 0.1	< 0.1	< 0.1
Zn	< 0.2	< 0.2	< 0.2
Anions (mg L^{-1}) — Leachate			
Sulfate	37	6.9	< 4
Chloride	< 50	< 50	< 50
Fluoride	0.1	< 0.1	5.7

WCS: Water Clarification Sludge. WSS: White Steel Slag. FIS: Furnace Iron Slag.

Regarding to WSS, it is characterized by a gray color (2.5Y 6/1) and an exceptionally high alkaline pH_{H2O} of 12.44, coupled with a remarkable electrical conductivity of 7.27 mS cm^{-1}. WSS showed an inorganic carbon content of 1.50 %, while organic carbon remained undetected. Despite having the lowest total nitrogen content among the tested wastes, WSS contained the highest levels of available phosphorus (22.8 mg kg^{-1}) and available potassium (151 mg kg^{-1}).

As for FIS, it is a gray-colored (10YR 4/1) waste material with an alkaline pH of 10.0 and low electrical conductivity (0.78 mS cm^{-1}). In terms of composition, FIS showed a total carbon of 1.70 %, with 1.00 % accounting for organic carbon, along with a total nitrogen content of 0.09 %. Moreover, the concentrations of available phosphorus and available potassium measured in this waste material measured 18.7 mg kg^{-1} and 56 mg kg^{-1}, respectively.

Each waste material displayed a distinctive chemical composition, indicative of its origin and treatment process. WCS had remarkably high concentrations of Al (> 10 wt%) due to the use of Al-based coagulants and the prevalence of aluminosilicate clay minerals, as revealed by XRD analysis. Its composition also included quartz, feldspars, iron oxides, and gypsum. On the other hand, WSS showed relatively higher levels of Ca (> 10 wt%) and Mg (6.67 wt%), suggesting its potential for soil improvement if used as alkaline amendment to raise the pH and reduce soil acidity. FESEM-EDS analysis revealed distinct metallurgical phases, with a notable presence of Ca primarily combined with Si, forming calcium silicate phases, which are significant in neutralizing acidity and removing trace elements from mine discharges (Fernández-Caliani et al., 2008). Additionally, calcite was identified, while Mg predominately occurred in the form of oxides and aluminates. FIS exhibited an elevated Fe content (7.56 wt%) in comparison to the other waste materials, due to the presence of poorly crystallized iron-silicate phases. Mineralogically, it was characterized by abundant quartz with minor anorthite and calcite, as crystalline phases identified by XRD analysis.

In contrast to the mine soil, the waste materials contained low total concentrations of potentially hazardous trace elements (Table 3). However, the presence of certain toxic elements, even at these reduced levels, such as 42 mg kg^{-1} of As in WCS and 294 mg kg^{-1} of Cu in FIS, raises concerns about their potential impact on soil and environmental quality before being used for land applications. Particularly worrisome is the potential for leaching elevated levels of trace elements, especially in agricultural and landscaping contexts (Siddique et al., 2010). Yet, elemental measurements of leachate from these wastes (Table 3) revealed negligibly low values, with concentrations falling below the detection limits for all reported elements (in mg L^{-1}): < 0.01 for Hg, < 0.05 for Cd, < 0.1 for As, Cu, and Pb, < 0.2 for Zn, and < 0.5 for Cr and Ni. Therefore, the waste materials used as amendments displayed a low potential for leaching contaminants, with none of the analyzed trace elements surpassing the soil solution concentration considered as toxic for vegetation establishment (Ross, 1996). The concentration of sulfate measured in the leach solutions was 37 mg L^{-1}, while chloride was found to be <50 mg L^{-1}, indicating a minimal presence of soluble salts. The concentrations of all dissolved cations and anions in the leachates adhere to the standards outlined in Spanish legislation for the formulation of Technosols derived from waste materials.

3.2. *Effects of waste amendments on chemical stabilization*

3.2.1. *Leachate quality*

The leaching test results (Table S1) provide valuable insights into potential pollutant release from Technosols. Fig. 2 graphically compares trace element concentrations leached from treated samples with the total contents in the untreated mine soil sample. The line chart in Fig. 2

enhances this comparison by depicting the proportion of the total trace element pool removed from the mine soil by leaching.

The untreated soil (sample PH-2) yielded highly acidic leaching solutions (pH = 2.5) resulting from the mine soil-water interaction, leading to varying degrees of solubilization of potentially toxic trace elements. Among these elements, Pb (26.16 mg kg^{-1}), Zn (4.94 mg kg^{-1}), and Cu (2.29 mg kg^{-1}) were the most prevalent in the leachates. Other deleterious trace elements, including As, Cd, Sb, Cr, and Ni, generally occurred at levels below 1 mg kg^{-1}. In contrast, leach solutions from the Technosols were moderately alkaline. The leaching of soluble divalent cations with low ionic potential, notably Cu^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+}, experienced a noticeable decrease with treatment. All waste amendments demonstrated the ability to reduce the mobility of these trace elements by at least 9.5, 8.3, 4.5, and 2.0, times respectively, with the Technosols S2T8–25 and S2T13–25 proving the most effective. Interestingly, Ni concentrations in most Technosol leachates exceeded

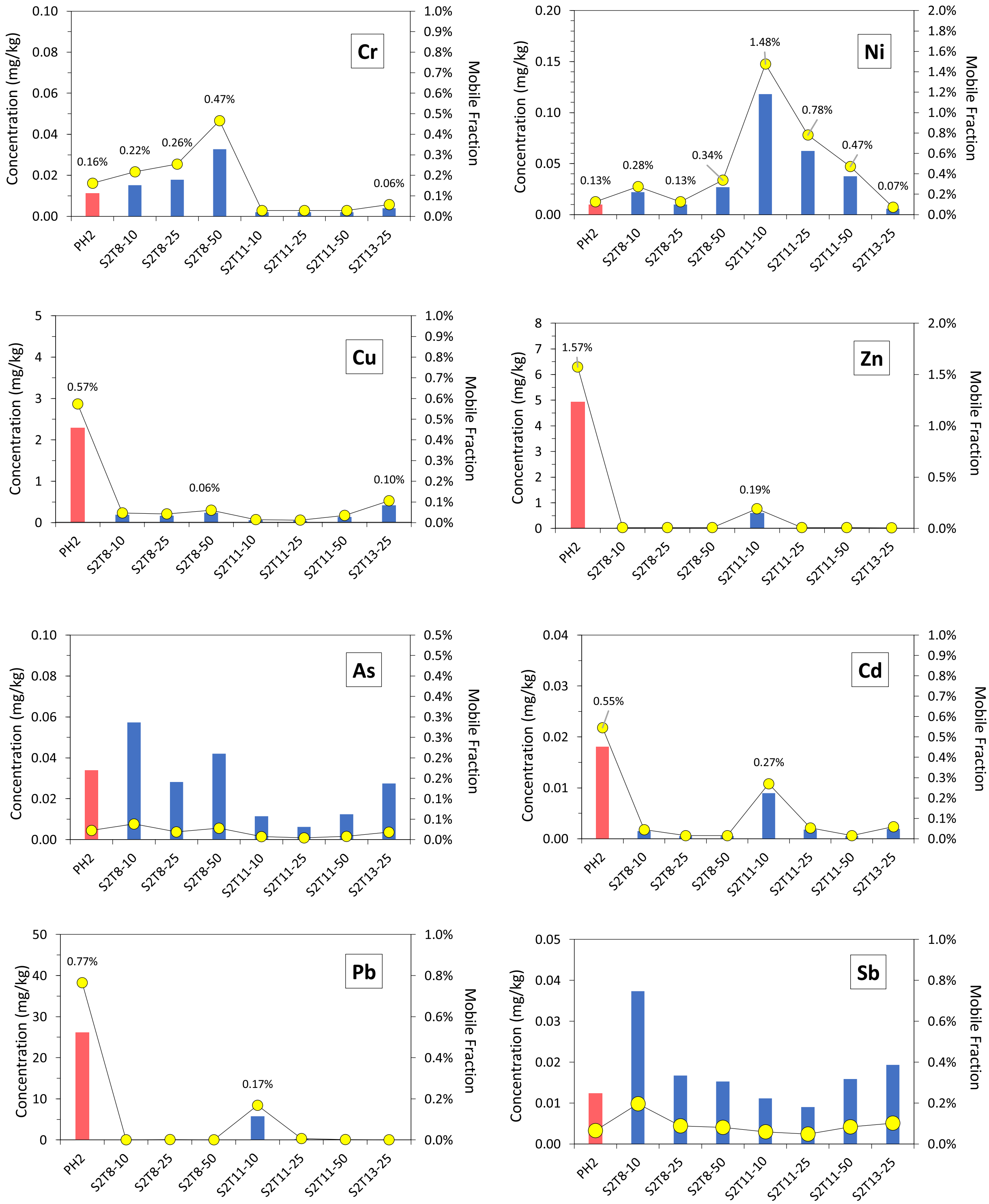

Fig. 2. Bar charts contrasting leaching concentrations of potentially toxic trace elements in untreated soil versus Technosols, and line charts showing the mobile fraction (%) released from the mine soil (sample PH2).

those in the control, attributed to the relatively high levels of this contaminant introduced by waste amendments, although the leaching fraction was limited to <1.5 %.

On the other hand, elements with high ionic potential, typically occurring as complex oxyhydroxy anions, such as As (up to 0.057 mg kg^{-1}), Cr (up to 0.033 mg kg^{-1}), and Sb (up to 0.037 mg kg^{-1}), showed increased concentrations in leachates from certain Technosols compared to those from untreated soil. This finding is consistent with the commonly noted observation that increased soil pH can weaken anion sorption onto soil minerals due to the increase in surface negative charge (Carabante et al., 2009). Nevertheless, these concentrations remained below regulatory limits (2 mg kg^{-1}, 10 mg kg^{-1}, and 0.7 mg kg^{-1}, respectively) established in Spain for Technosols derived from waste materials. Moreover, the leachable fraction of trace elements was negligibly low, with maximum release values of 0.47 % for Cr, 0.20 % for Sb and 0.04 % for As.

3.2.2. *Soil pore water chemistry throughout the pot experiment*

Despite significant reduction in trace element leachability from most treatments, formulations S2T8–25 and S2T13–25 were selected as first choices for a growth test in a pot experiment with *B. juncea*. As contaminants are primarily taken up by plant through the root system, analyzing the interstitial water in soil pores provides valuable insights into of trace element availability and a more accurate indication of environmental risk (Nolan et al., 2003). Therefore, the concentration of trace elements in the soil solution, extracted using Rhizon samplers, holds particular importance as it represents the fraction of soil water available for plant uptake (Clemente et al., 2008).

The Technosol-based treatment significantly influenced the pH, electrical conductivity, and redox status (Eh) of the soil-water system. The soil solution extracted from the untreated control soil showed extremely acidic pH values, ranging from 1.8 to 2.4 (Fig. S1a), nearly matching or slightly lower than the soil pH measured in water. This acidity persisted throughout the entire experimental period. Technosol S2T8–25 treatment initially shifted pore water pH from extremely acidic to slightly acidic (pH = 6.6), maintaining an alkaline level consistently. Technosol S2T13–25 induced initial acidity, with pH values around 4 in the first month of treatment, stabilizing at near-neutral values (pH = 6.7–6.8) after three months. The pH variations in both Technosols arise from complex interactions between the amendments and the mine soil, with the higher acid-neutralizing capacity of WSS playing a substantial role in determining pH trends. The pH increase in Technosols was significant compared to the control soil ($p < 0.00008$). The application of the highest dose of WSS not only induced a rapid pH increase in the Technosol S2T8–25 (40 % WSS) compared to Technosol S2T13–25 (16.66 % WSS) but also sustained an acid-neutralizing action throughout the four-month trial. Hence, the Technosol treatment efficiently neutralized the acid generated (104 mmol H^+ kg^{-1}) by the mine soil, fostering a more conducive environment for plant growth.

The pore water extract from the untreated mine soil initially had an electrical conductivity of 26.7 mS cm^{-1}, decreasing over time to recorded values (15.6–17.8 mS cm^{-1}) in the second month of treatment and thereafter (Fig. S1b). This decline in leachate conductivity, attributed to the dissolution and washing out of sulfate salts, is consistent with the presence of a finite pool of readily soluble sulfate for release. Similarly, the Technosols showed decreasing electrical conductivity over time, ranging from 21.0 mS cm^{-1} to 7.9 mS cm^{-1} (Technosol S2T13–25) and from 12.0 mS cm^{-1} to 6.7 mS cm^{-1} (Technosol S2T8–25). The treatment significantly reduced electrical conductivity compared to the control soil ($p < 0.004$), reflecting a decrease in sulfate concentration in the soil solution. Therefore, the observed decline in electrical conductivity values following treatment was another noticeable effect of the applied waste amendments.

The initial soil solution extracted from the mine soil showed a redox potential of 717 mV, indicating highly oxidizing conditions. Following waste amendment application, the Eh decreased to 398 mV in Technosol S2T8–25 and 528 mV in Technosol S2T13–25 two weeks later. At the end of the pot experiment, the pore water extracts exhibited Eh values of 370.4 ± 0.9 mV and 372.1 ± 1.9 mV, respectively, indicating a shift to moderately oxidizing conditions. In contrast, the mine soil control remained under oxidizing conditions with an Eh of 695 mV.

Rising soil pH and maintaining oxidizing conditions had a beneficial impact on soil pore water quality by boosting the retention of trace elements through chemical stabilization processes (Basta and McGowen, 2004; Kumpiene et al., 2008; Bolan et al., 2014). These immobilization mechanisms led to the redistribution of contaminants from the soil solution to the solid phase, thereby reducing their bioavailability and phytotoxicity for the restoration of vegetation. Concentrations of trace elements in pore water extracts from both treated and untreated (control) soil samples are listed in Table S2, and graphically depicted in Fig. 3 for comparison. The application of Technosol buffered the soil pH to moderately alkaline (Technosol S2T8–25) or near-neutral (Technosol S2T13–25) values, enhancing the attenuation of trace element contaminants.

Remarkably, there was a significant and substantial decrease in the dissolved metal(loid) load of the Technosols compared to the untreated soil ($p < 0.05$). Concentrations of all measured trace elements in the pore water extracts dropped by several orders of magnitude owing to the treatment-induced rise in pH. This reduction was particularly pronounced for trace elements influenced by pH, displaying their lowest mobility within the neutral to slightly alkaline range. For instance, the concentrations of initially dissolved Cu and Zn in the mine soil solution dropped from 481.1 mg L^{-1} and 789.9 mg L^{-1}, respectively, to <1 mg L^{-1} by the end of the four-month monitoring period. Therefore, the alleviation of soil acidity was a major factor driving the immobilization of metallic cations by reducing the activity hydrogen ions in the soil solution, thereby minimizing their competition for metal binding sites. Mineral saturation indices computed with PHREEQC revealed that the addition of waste amendments to mine soil triggered the precipitation of various Cu-bearing phases, especially copper ferrite ($CuFe_2O_4$) (SI = 12.8–16.9), and carbonates like azurite ($Cu_3(CO_3)_2(OH)_2$) (SI = 1.3) and malachite ($Cu_2(CO_3)(OH)_2$) (SI = 2.0) in Technosol S2T8–25, indicating reduced mobility but allowing potential plant uptake upon re-acidification. Conversely, minerals bearing Cd, Pb, or Zn, did not exhibit positive SI values, suggesting that their dissolved concentrations were controlled most likely by adsorption rather than precipitation.

Despite the potential risk of As mobilization associated with the pH increase to the alkaline region (Hartley et al., 2004; Kumpiene et al., 2008), the soluble concentrations of As interestingly dropped from 38.27 mg L^{-1} to either 23 μg L^{-1} (Technosol S2T8–25) or 8 μg L^{-1} (Technosol S2T13–25) by the end of the observation period. Clearly, this reduction in the concentration of As and other trace elements suggests a potential decrease in the mobility and phytoavailability of these potentially harmful elements. In Technosol S2T8–25, the decline in As mobility cannot be solely attributed to the adsorption of soluble oxyanion species, as the negatively-charged surfaces of soil particles increased after acid neutralization. Instead, it might be linked to the precipitation of low-solubility As-Ca complexes (Bothe and Brown, 1999; Porter et al., 2004; Fernández-Caliani et al., 2022).

On the other hand, concentrations of key major elements such as Al, Fe, and S in the pore water of the Technosols were significantly lower ($p < 0.004$) than in the control soil. Remarkably, the soluble concentration of Al dramatically dropped from 5200 mg L^{-1} to undetectable levels, mitigating one of the most severe toxicity issues in acid mine soils (Fernández-Caliani and Barba-Brioso, 2010). Potential control over the solubility of dissolved Al within the pH range of 6–9 may arise from the formation of aluminum hydroxide solid phases (Sánchez-España et al., 2011). Saturation indices predicted by PHREEQC for gibbsite ($Al(OH)_3$) (SI = 2.75), boehmite (γ-AlOOH) (SI = 2.46), and diaspore (α-AlOOH) (SI = 4.16) indicate that the reduction in dissolved Al concentrations was likely governed by the precipitation of aluminum hydroxide phases, which provides the soil with additional sorption capacity.

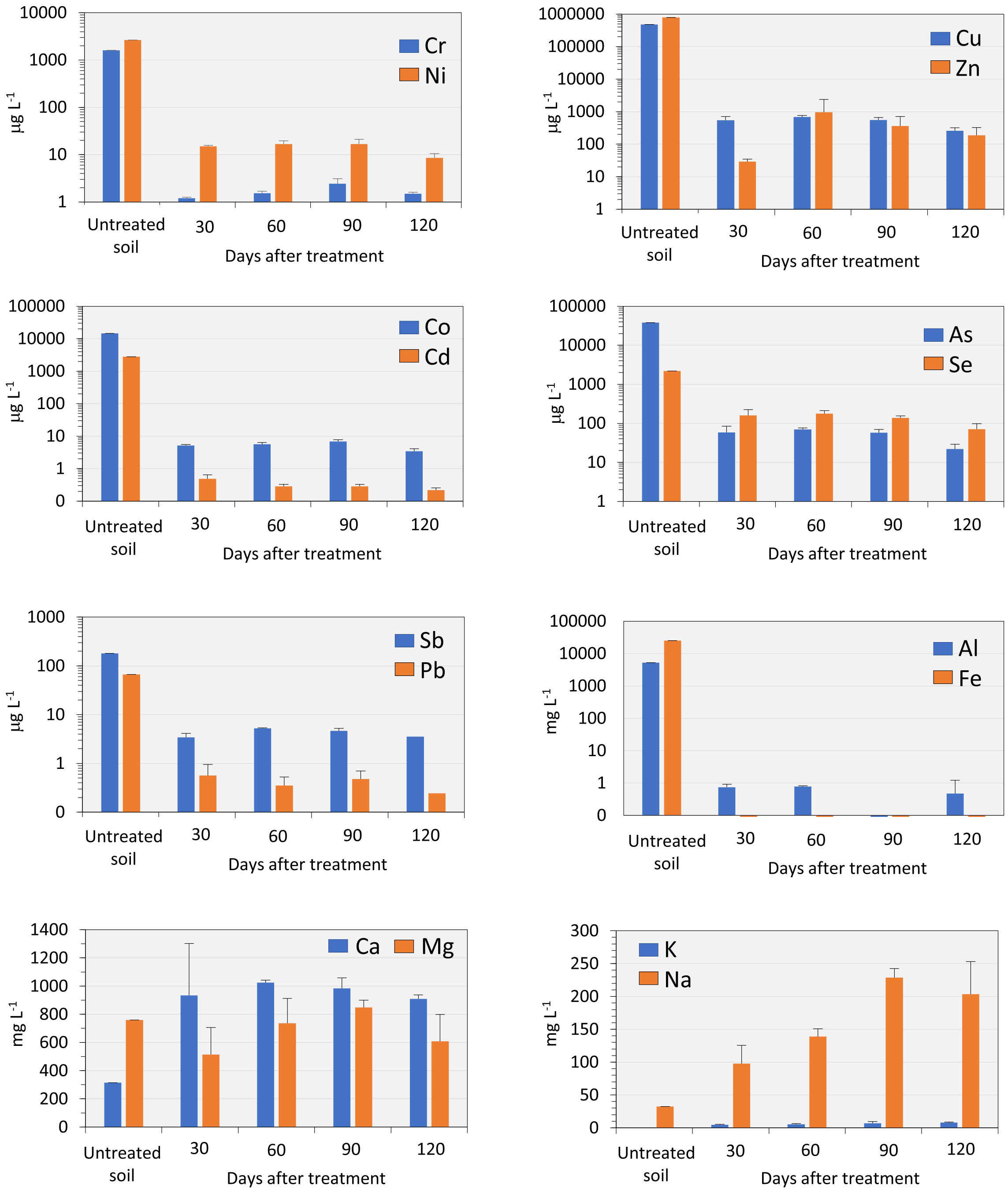

Fig. 3. Comparative bar charts displaying element concentrations in the untreated mine soil (control) and the Technosol S2T8–25. Error bars denote the standard deviation of the means ($n = 3$).
Fig. 3 (continued). Comparative bar charts displaying element concentrations in the untreated mine soil (control) and the Technosol S2T13–25. Error bars denote the standard deviation of the means (n = 3).

Moreover, a fraction of trace elements may have been removed from the soil solution and sequestered by newly-formed hydrous ferric oxides (HFO) through adsorption, complexation and (co)precipitation processes (Carlson et al., 2002; Sherman and Randall, 2003). HFO surfaces are known to be involved in As adsorption in soils (Waychunas et al., 1993; Hartley and Lepp, 2008; Kumpiene et al., 2021). Equilibrium speciation calculations revealed supersaturation concerning ferrihydrite ($Fe_{10}O_{14}(OH)_2$) (SI = 3.8), which is thermodynamically unstable and can be transformed to either lepidocrocite (γ-FeOOH) or goethite (α-FeOOH). Hence, it can be inferred that these HFO precipitates played a pivotal role in controlling iron activity in the soil solution of both Technosols. This is consistent with the significant reduction in water-soluble Fe concentrations, decreasing from 25 g L^{-1} to values below 1 mg L^{-1}. The most likely HFO precipitate under neutral or mildly alkaline pH conditions is ferrihydrite, a nanocrystalline phase commonly found in ochreous precipitates from Fe-rich surface waters with a pH >5 (Bigham et al., 1992; Murad and Rojík, 2003). Consequently, HFO surfaces might have efficiently removed contaminants from the soil solution through adsorption and co-precipitation mechanisms.

In contrast, concentrations of Ca, Mg, Na, and K in the soil solution

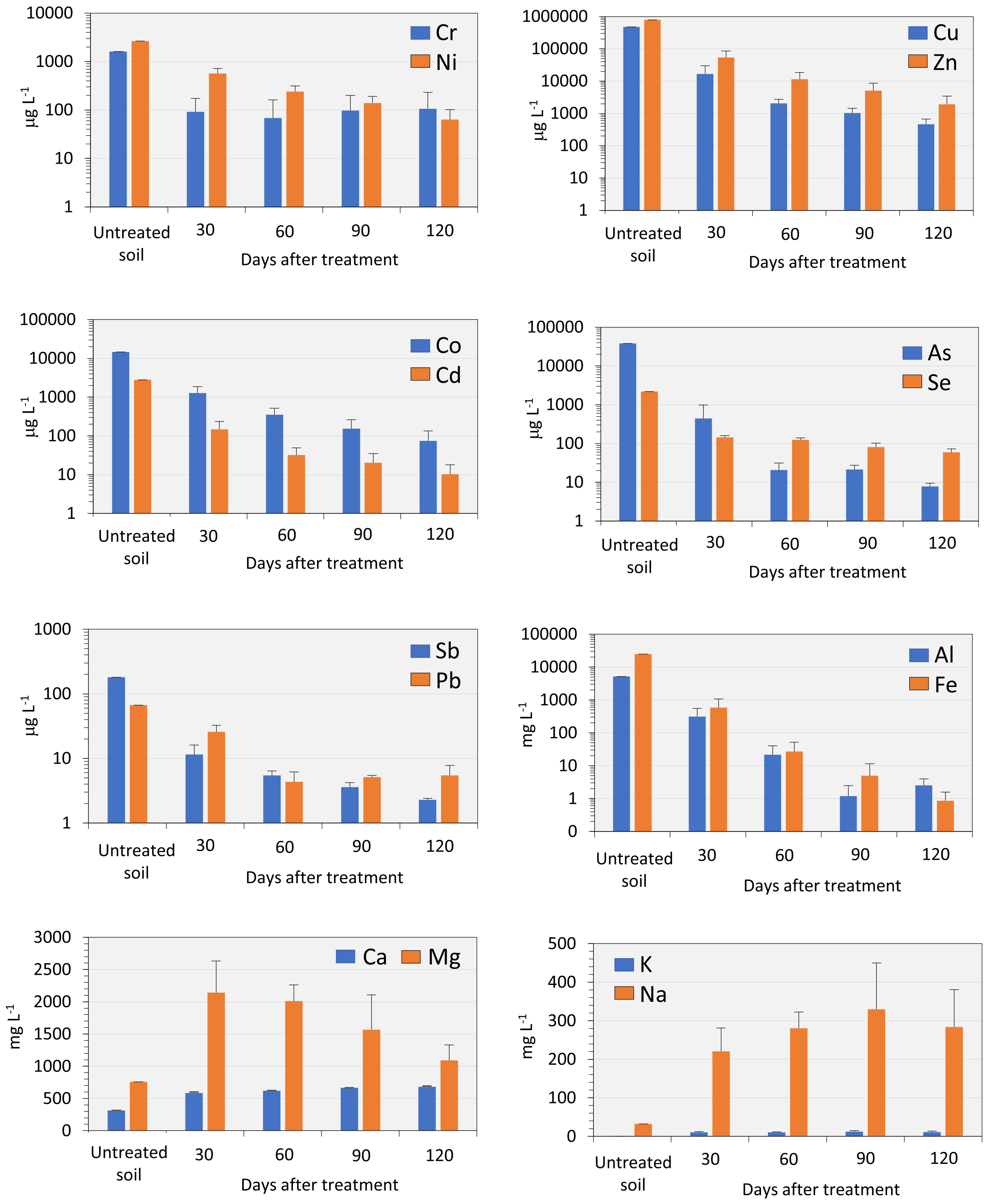

Fig. 3. (*continued*).

showed a significant increase compared to the control ($p < 0.01$). Technosol application led to an increase in soluble Ca content from to 315 mg L^{-1} (control soil) to 1024 mg L^{-1} (S2T8–25) and 683 mg L^{-1} (S2T13–25). Furthermore, there was an increase in soluble Mg content, particularly in S2T13–25 (from 760 mg L^{-1} up to 2141 mg L^{-1}), although the Mg concentration gradually decreased over time to 1089 mg L^{-1}. The minerals most prone to dissolution in the waste amendments were notably calcite, but also calcium silicate compounds, as well as magnesium oxides and aluminates. This boost in the solubility of essential nutrients was advantageous for promoting soil fertility and vegetation establishment.

Concerning anions (Fig. S2), sulfate stood out as the dominant species in all pore water solutions, initially reaching a concentration of 82.95 g L^{-1} in the untreated soil. Over time, this concentration significantly decreased to 22.45 g L^{-1} due to the washing out of efflorescent sulfate salts formed on the topsoil. During the experiment, the addition of water to restore moisture content resulted in the dissolution of sulfate salts, with partial reprecipitation observed on the pot walls of the control sample. Conversely, higher concentrations of chloride (up to 1509 mg L^{-1}), nitrate (up to 122 mg L^{-1}), and fluoride (up to 44 mg L^{-1}) were detected in the extract soil solutions of the Technosols compared to the untreated mine soil. Moreover, the concentration of bicarbonate anions in pore water emerged as a notable species following the Technosol-based treatment, peaking at 866 mg L^{-1}. This substantial increase was most pronounced and sustained at the higher dose of WSS (Technosol S2T8–25).

On the other hand, the rise in pH induced by the waste amendment to alkaline levels might theoretically destabilize metal-bearing minerals like jarosite, impacting soil acidity and triggering the re-release of sulfate and trace elements back into the soil solution (Hudson-Edwards et al., 1999). However, this potential concern does not appear to be supported by the data, as indicated by consistently low concentrations of Fe, sulfate, and K in the pore water extracts of the Technosols throughout the entire pot experiment.

3.2.3. Soil solution speciation modeling

Understanding the mobility, availability, and toxicity of contaminants in the soil solution, requires a focus on trace element speciation rather than total dissolved concentration (Kalis et al., 2008). PHREEQC speciation calculations provided insights into the distribution of trace element of concern among various chemical species in both untreated soil and Technosols after the four-month pot trial (Fig. 4).

In untreated soil, aluminum was mainly associated with sulfate ions, existing in monomeric ($AlSO_4^+$) and dimeric ($Al(SO_4)_2^-$) forms, with free ions comprising about 6 % of the dissolved fraction. The highly toxic Al^{3+} form poses a significant limitation for plant growth (Chandra and Keshavkant, 2021). Waste amendments prompted a shift towards hydroxylated species, particularly with $Al(OH)_4^-$ being the dominant aqueous species in both Technosols. In this state, aluminum is less toxic to plant roots. Predicted $Al(OH)_3$ suggests some aluminum hydroxide precipitation, and $Al(OH)_2^+$ in Technosol S2T13–25 does not exhibit phytotoxicity under slightly acidic conditions (Bojórquez-Quintal et al., 2017). The rise in pH likely alleviated aluminum toxicity by rendering it less soluble and more prone to form less toxic species. Consequently, nutrient availability to plants improved as competition for root uptake sites with toxic Al^{3+} ions decreased.

Trace element speciation was clearly dominated by sulfate complexes and free (uncomplexed) ions. Specifically, Cu, Cd, Pb, and Zn were predicted to be associated mainly with sulfate anions, forming prevalent species such as $CuSO_4$, $Cd(SO_4)_2^{2-}$, $Pb(SO_4)_2^{2-}$, and $Zn(SO_4)_2^{2-}$, respectively. Furthermore, remarkable concentrations of free ions, accounting for 45 % Cu^{2+}, 16 % Cd^{2+}, 11 % Pb^{2+}, and 15 % Zn^{2+} of the

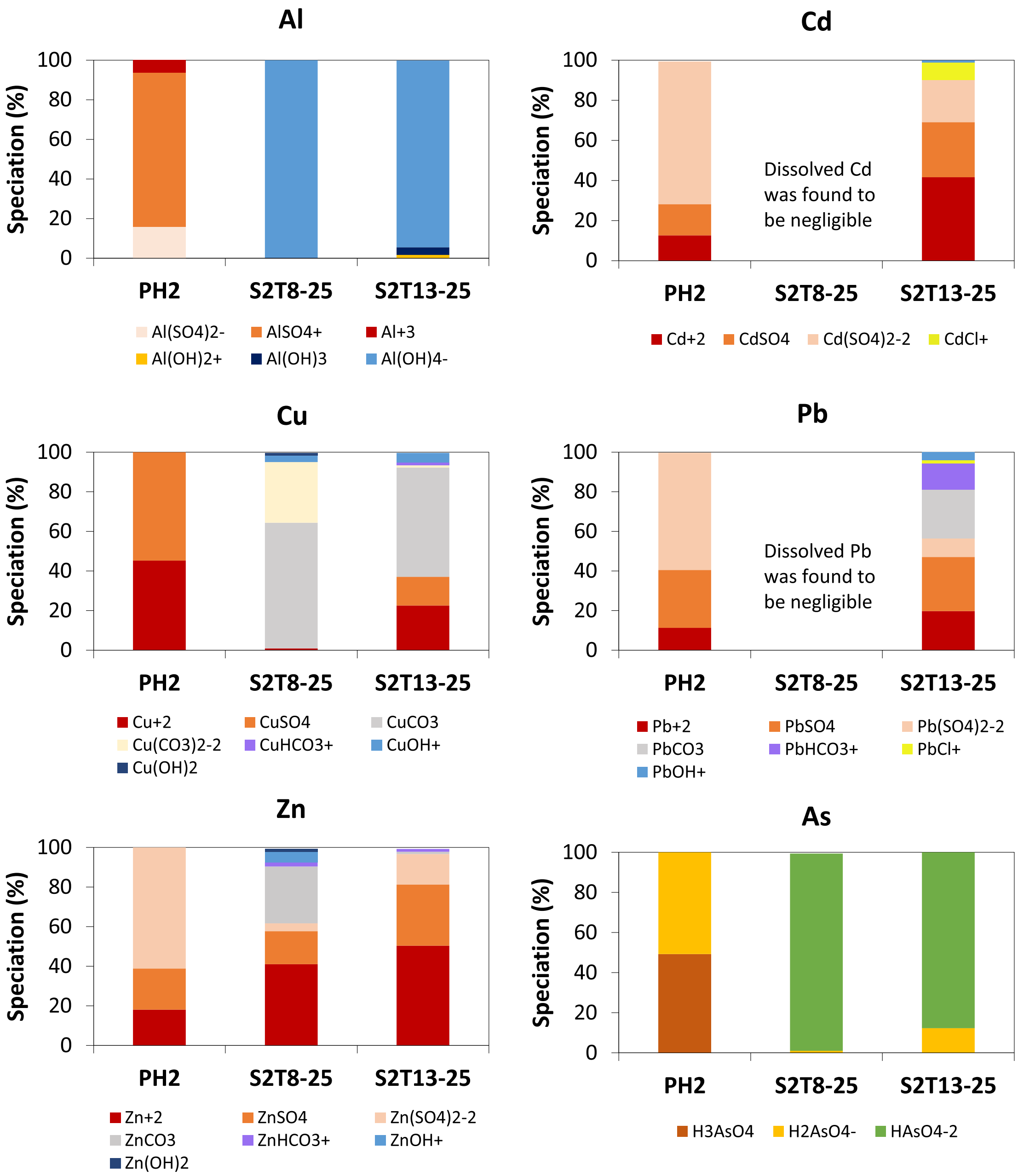

Fig. 4. Predicted speciation of trace elements of concern in the soil solution.

dissolved fraction, had the potential to induce phytotoxicity and hinder plant growth (Kumar et al., 2021).

The Technosol-based remediation approach induced substantial alterations in chemical speciation, resulting in a diverse distribution of species (hydroxide, carbonate, bicarbonate, chloride, sulfate, and free ions), which had a significant impact on trace element mobility and plant availability. Copper speciation was dominated by $CuCO_3$ in both Technosols, contributing to a favorable environment for plant growth by decreasing the activity of toxic Cu^{2+} ions. Lead speciation exhibited a mix of carbonate, sulfate, free ions and other soluble complexes with inorganic ligands. Zinc displayed a variety of species, including, sulfate, carbonate, and free ions. Meanwhile, Cd primarily existed as free Cd^{2+}, sulfate complexes, and chloride ions. Shifts in Pb and Zn speciation suggest decreased mobility, influencing plant availability, though a fraction of free Zn^{2+} ions remained available to plants. Similarly, the proportion of free Cd^{2+} ions in Technosol S2T13–25 raises concerns about plant uptake risk, and the occurrence of $Cd(SO_4)$ and $Cd(SO_4)_2^{2-}$ suggests limited changes in Cd speciation compared to untreated soil.

Arsenic speciation shifted towards less toxic forms ($HAsO_4^{2-}$) due to increased pH and oxygenation, thereby contributing to improved soil health. Oxidized forms of As(V) prevailed in the soil solution, aligning with positive and high measured values of Eh. Initially, As existed in the untreated mine soil in nearly equal distribution as arsenous acid (H_3AsO_4) and dihydrogen arsenate ($H_2AsO_4^-$). However, the treatment induced a significant shift towards the dominance of hydrogen arsenate ($HAsO_4^{2-}$), with a slightly higher proportion of dihydrogen arsenate ions in S2T13–25 compared to S2T8–25. The rise in soil pH and maintenance of an oxygenated environment enhanced the prevalence of $HAsO_4^{2-}$, which is typically less mobile than H_3AsO_4 and $H_2AsO_4^-$, and much less toxic than arsenite species (Yamauchi and Fowler, 1994).

Substantial changes in chemical speciation, particularly of Al, Cu, and As, and the saturation status of the soil solution indicate that Technosol treatment effectively transformed soil pore water chemistry. Reduced dissolution potential of metal-bearing minerals may contribute to improving soil health by minimizing the release of potentially toxic contaminants bound to such phases. Ultimately, these modifications may enhance nutrient cycling and availability, aligning with the goal of mitigating trace element toxicity and fostering overall soil conditions for plant growth.

3.3. *Effects of waste amendments on plant establishment and growth*

Mine soils pose significant obstacles to conventional direct sowing practices due to their inherently challenging environmental conditions (e.g. Arenas-Lago et al., 2022; Carvalho et al., 2022; Mourinha et al., 2022), including elevated trace element content, acidic pH, and poor nutrient availability. These factors impede the establishment of sustainable plant populations, leading to limited success with direct sowing methods. As a result, alternative approaches such as the transplantation of pre-treated seedlings in controlled environments have shown promising potential in revegetating abandoned mine lands (Fernández-Caliani et al., 2021). Additionally, hydroseeding techniques have been used to enhance vegetation cover on slopes of waste rock piles (Madejón et al., 2021). To address these challenges, our study intentionally adopted a germination test in seedbeds as a preliminary step before transplanting into pots. This approach aimed to evaluate seed viability and initial growth, given the adverse soil conditions and potential limitations of direct sowing. The validity of this strategy is supported by findings from previous studies that have employed similar germination tests (e.g. Rodríguez-Vila et al., 2014, 2016; Baragaño et al., 2021).

The germination assay conducted on *B. juncea,* assessing seed viability and the suitability of the Technosols for seedling establishment, yielded distinct outcomes. As expected, seeds in the untreated mine soil failed to germinate due to various constraints for plant life, including strong acidity, nutrient scarcity, high pollution load, and contaminant phytotoxicity. It is noteworthy that, this Fe-rich acidic soil at the mine site is currently barren due to severe degradation (Fernández-Landero et al., 2023). In contrast to the untreated soil, germination and seedling growth of *B. juncea* were observed in Technosols. The seeds sown on Technosols successfully hydrated, sprouted and developed fully expanded cotyledons within a week. Seeds were deemed to have germinated when the emerged radicle reached at least 3 mm in length (ISTA, 2005). Thus, the percentages of seed germination varied across treatments (Fig. 5a): untreated mine soil (0 %), Technosol S2T13–25 (56.7 %), Technosol S2T8–25 (86.7 %), and mulch control (90 %).

Fig. 6 illustrates the evolution of *B. juncea* plants during the four-month pot trial. All seedlings transferred to pots filled with Technosols S2T8–25 and S2T13–25 developed true leaves after a week, but remarkable differences were observed between the treatments in terms of plant establishment and vegetative growth. In Technosol S2T8–25, all plants survived until week 11, with four persisting by week 12 (Fig. 5b). By the end of the experiment, two plants were still thriving, yielding a 40 % survival rate, which was comparable to the seedlings in the mulched control pot. This suggests the success of waste amendments in promoting plant adaptation and resilience. The plants grew to an average maximum height of 5.7 cm during weeks 7 and 8, maintaining a stable height of 4.5–5 cm until the end of the observation period (Fig. 5c). The height of the plant after four month of growth in the mulched control pot was 8.5 cm. *B. juncea* displayed leaves with an alternate arrangement, elongated shapes, and serrated margins. The leaf count per pot (Fig. 5d) varied from 19 (week 5) to 6 (week 16), while in the mulched reference pot it ranged between 23 (weeks 10 and 11) and 4 (week 16).

In Technosol S2T13–25, one out of the initially planted five plants died at the early seedling stage (80 % survival rate). By week 7, only one plant remained, accounting for a 20 % survival rate, and by week 12 all plants died, indicating a reduced capacity for *B. juncea* to thrive in this Technosol. These plants attained an average peak height of 3.1 cm during weeks 4 and 5. Beyond week 7, a distinct inhibition in plant growth became apparent by reduced height and leaf expansion. The decline in growth can be traced to the demise of larger plants, shedding mature leaves, and the emergence of smaller leaves that failed to reach previous heights. The leaf count per pot peaked at 14 in week 4. Compared to plants in the mulch control pot, *B. juncea* in Technosol S2T13–25 showed stress-related morpho-physiological effects, including stunted growth, development of small leaves, delayed maturity, and foliar chlorosis, resembling symptoms of nutrient deficiency and metal stress (Chandra and Keshavkant, 2021; Kumar et al., 2021).

The results clearly establish Technosol S2T8–25, which combines 60 % WCS and 40 % WSS, as the superior choice for fostering the growth of *B. juncea*. This conclusion is supported by a higher survival rate, greater average height, and a more consistent leaf count observed in this Technosol compared to Technosol S2T13–25 (*t*-test, $p < 0.05$). Plants grown in Technosol S2T8–25 also exhibited healthy growth characteristics, while those in Technosol S2T13–25 displayed signs of stress. The higher concentration of potentially toxic elements in the pore water of Technosol S2T13–25 (t-test, $p < 0.05$) may account for the reduced survival rate, stunted growth, and chlorosis observed in plants grown in this Technosol. In contrast, Technosol S2T8–25 showed a significantly lower concentration of potentially toxic elements and a higher concentration of Ca and bicarbonate ions in the pore water of (t-test, $p < 0.035$). By neutralizing acidity, the addition of WSS not only mitigated the potential risk of metal toxicity but also increased the availability of Ca and other essential nutrients, suggesting that the chemical environment of Technosol S2T8–25 was more conducive to plant growth and resilience.

However, larger-scale field trials may be necessary to assess Technosols under more realistic conditions. The effectiveness of Technosols may vary depending on the plant species being grown. Studies with a wider range of plant species are needed to fully understand the range of potential applications for Technosols.

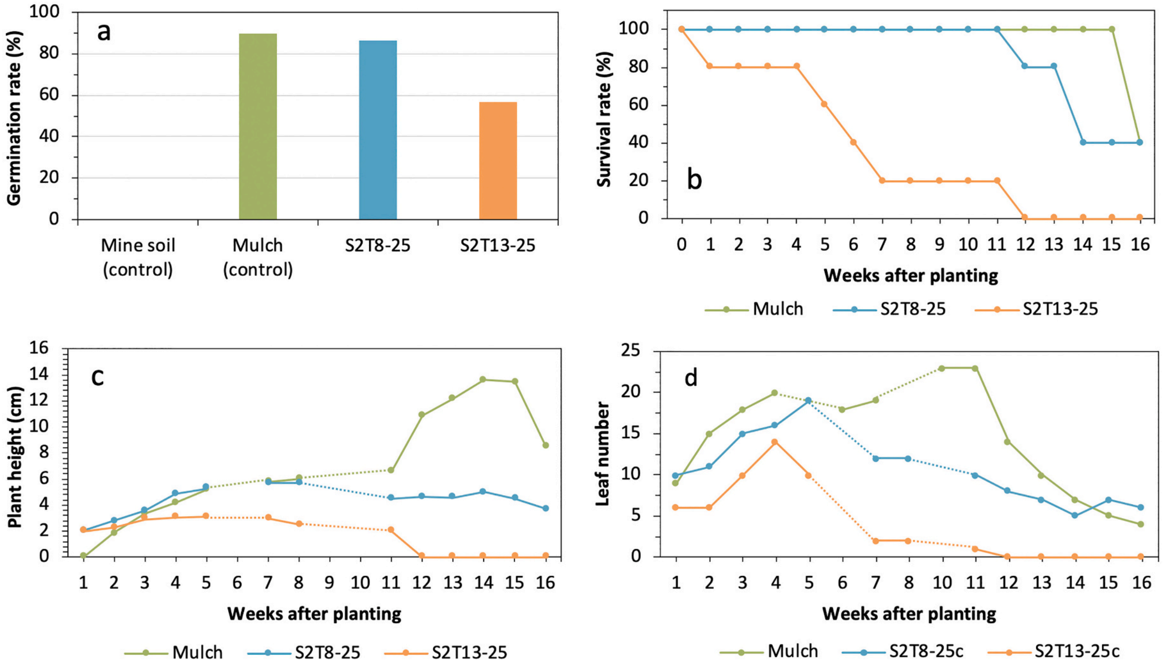

Fig. 5. Temporal dynamics of essential *Brassica juncea* plant parameters in formulated Technosols and control settings: (a) seed germination rate; (b) survival rate; (c) plant height; and (d) leaf number.

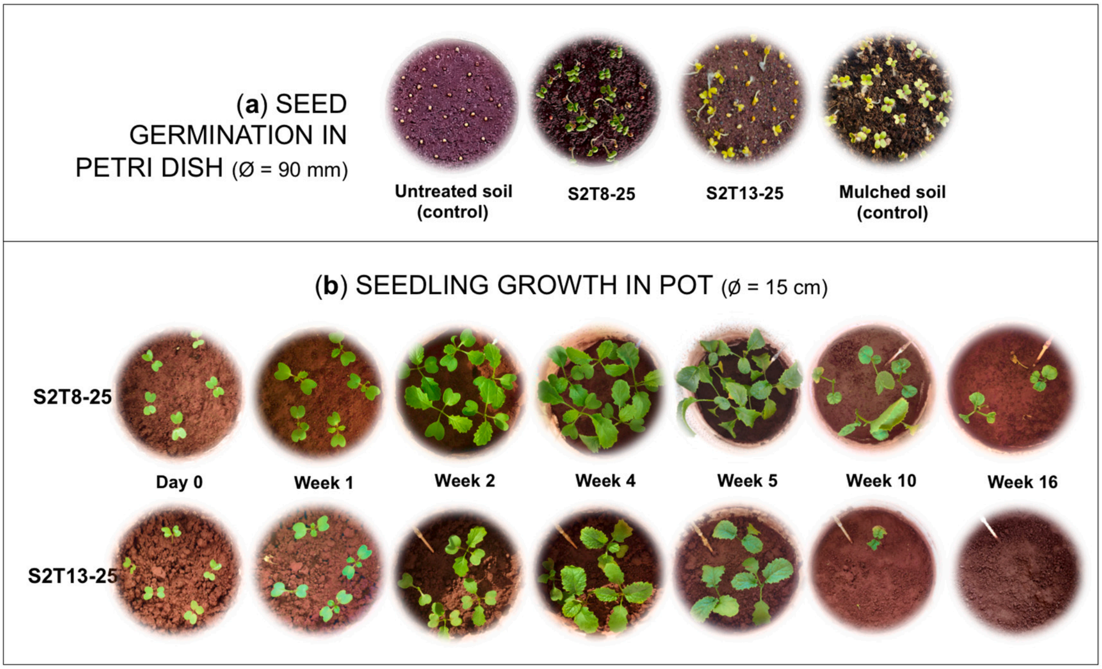

Fig. 6. Visual comparison of *Brassica juncea* outcomes in terms of: (a) seed germination assay; and (b) seedling growth in pots.

3.4. Potential for plant growth in Martian-like soil

The barren and harsh conditions of the Fe-rich acidic soil at the Rio Tinto site mirror challenges faced by plants in Martian soil simulants, marked by limited nutrient availability and potential toxicity. An examination of the red mine soil from the Rio Tinto Mars analog site reveals significant constraints to vegetation establishment, including: strong acidity, lack or deficiency of organic matter and essential nutrients, soil salinity due to high soluble sulfate content, and elevated concentrations of metallic cations dissolved in the soil solution. This complex interplay of acidic conditions, heightened trace element and sulfate levels, and nutrient deficiencies creates an inhospitable environment for plant growth, requiring a remediation strategy to overcome such limitations for successful germination and seedling growth.

The results of the germination assay indicate promising potential for *B. juncea* establishment and growth in Technosols compared to untreated mine soil. The failure of seeds to germinate in the mine soil underscores its hostile conditions. Plant growth and trace element availability were highly influenced by soil pH, as observed in soils contaminated with pyrite sludge (Clemente et al., 2005). Aluminum, considered a potential growth-limiting factor in acidic environments, causes rhizotoxicity by inhibiting nutrient transportation (Chandra and Keshavkant, 2021). On Mars soil simulants, many germinated plants died or remained stunted due to low pH and the presence of free Al^{3+} ions (Wamelink et al., 2014).

In contrast, Technosols, notably S2T8–25, demonstrated substantial improvement, with 87 % germination rate, showcasing the effects of waste amendments on overcoming soil constraints. The subsequent pot experiment further confirmed the positive impact of waste amendments on supporting *B. juncea* growth by enhancing soil conditions. Successful germination, plant survival, and plant growth in Technosol S2T8–25 underlines the effectiveness of the Technosol construction approach in creating a conducive environment for plant establishment. The development of true leaves, coupled with a considerable survival rate and stable plant height, indicates improved soil fertility achieved through waste amendment addition. While the organic matter and assimilable P and K provided by WCS enhanced soil fertility, conditioner amendments, notably WSS, not only contributed effective acid neutralization capacity through base cation leaching, but also increased the availability of Ca, Mg, K, and Na to plants.

Positive outcomes in Technosol S2T8–25 highlight the potential of waste amendments for long-term buffering against acidification, improving soil fertility, and immobilizing contaminants, thus contributing to a more hospitable environment for plant growth. The waste amendment combining 60 % WCS and 40 % WSS proved the most effective, resulting in *B. juncea* grown with the highest biomass. However, Technosol S2T13–25 posed challenges in plant adaptation and growth, as indicated by the reduced survival rate, suggesting a need for further refinement in waste amendment composition to optimize plant growth. The observed growth inhibition, characterized by a decline in height and leaf expansion, emphasizes the importance of tailoring waste amendments to specific soil conditions.

In summary, the findings support the hypothesis that waste amendments in Technosols can address the factors limiting plant growth in Martian-like soil, such as the Fe-rich acidic mine soils of Rio Tinto. Overall, the success of Technosols in remediating challenging mine soils and supporting plant growth in Martian-like soils suggests their potential to transform extreme environments into habitable and productive spaces. Nevertheless, the variability in results between Technosols implies that the composition and characteristics of the amendments require careful consideration. The observed differences provide valuable insights into the complex interplay between waste amendments and soil-plant interactions, guiding future efforts in sustainable mine land reclamation.

4. Conclusions

This study delved into the complex and dynamic interactions among mine soil, waste amendments, soil water chemistry, and plant responses to assess the efficacy of the Technosol-based approach in revegetating iron-rich acidic mine soils, such as those at the Rio Tinto Mars analog site. The acidic and heavily polluted soil pore water posed challenges to plant growth, but the synergistic effects of waste amendments successfully stabilized contaminants and supported plant growth. The treatment not only alleviated acidity but also reduced trace element concentrations to environmentally sustainable levels, supplying essential nutrients for plant development. Copper removal from the soil solution occurred through precipitation reactions, while the immobilization of As and other trace elements likely took place through adsorption onto or co-precipitation with newly formed Fe oxy-hydroxides and Al hydroxides. Predicted changes in aqueous chemical speciation indicated effective modification of soil pore water chemistry, reducing trace element toxicity and mitigating environmental risks.

Pot experiment with *B. juncea* showcased plant adaptability and resilience under stressful soil conditions, offering valuable insights into potential challenges and strategies for plant growth in Martian soil simulants. While positive impact on seed germination and seedling growth was evident, differential responses between Technosols emphasize the importance of optimizing waste amendment composition achieve optimal plant growth. Acknowledging hurdles like long-term performance and site-specific considerations, results suggest Technosols as a promising avenue for assisted natural remediation in managing similar mining-contaminated soils. Finally, to validate the approach and ensure lasting stability in immobilized contaminants and sustained plant life under actual field conditions, further research and field trials would be justified.

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CRediT authorship contribution statement

Juan Carlos Fernández-Caliani: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Sandra Fernández-Landero:** Writing – review & editing, Visualization, Software, Resources, Investigation, Formal analysis, Data curation. **María Inmaculada Giráldez:** Writing – review & editing, Validation, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Data curation. **Pablo J. Hidalgo:** Writing – review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition, Formal analysis. **Emilio Morales:** Writing – review & editing, Validation, Software, Methodology, Investigation, Formal analysis.

Declaration of competing interest

Juan Carlos Fernandez-Caliani reports financial support, equipment, drugs, or supplies, and travel were provided by Regional Government of Andalusia (Spain). Juan Carlos Fernandez-Caliani reports equipment, drugs, or supplies and travel were provided by DSM Soluciones Medioambientales. Pablo J. Hidalgo reports financial support provided by EU project 101071300 Sustainable Horizons. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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