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SOIL SUSTAINABILITY AND INNOVATION

Development of sustainable hydromorphic Technosols within artificial wetlands in mining landscapes: the effects of wastewater and hydrothermal geological materials

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Abstract

Purpose The Buenavista del Cobre mine is in a semiarid environment in NW Mexico. A part of the mine tailings dam has been flooded with wastewater from Cananea, generating an artificial wetland. The main objectives of this work were to evaluate the effect of wastewater on the pedogenesis of wetland Technosols developed on mine tailings and to compare them with the soil of non-irrigated tailings and with a natural soil profile.

Materials and methods Three profiles were studied inside the dam as follows: a profile under waterlogging conditions, a profile under conditions of periodic sewage saturation, and a profile with no waterlogging conditions. Laboratory methods included the micromorphological analysis of the soil structure and pedo-features, fertility properties, identification of clay minerals, and analysis of bulk chemical composition.

Results and discussion It was found that the biogenic structure and voids associated with organic materials were the main micromorphological features of the studied wetland Technosols. Primary sulfides remained unaltered in the Technosols irrigated with wastewater, whereas incipient sulfide oxidation was observed in the non-irrigated tailings. Chlorite and smectite were detected in the Technosols. Such mineral assemblage was found to be mostly generated by hydrothermal processes.

Conclusion Irrigation of tailings with wastewater supported the biological aggregation and porosity formation within the soil matrix, supplied plant nutrients, and enhanced the ecological soil quality of the studied hydromorphic Technosols. Saturation with wastewater hampered the oxidation of primary sulfides in the hydromorphic Technosols, preventing soil acidification and the mobilization of heavy metal contaminants.

Keywords Hydrothermal · Clay minerals · Soil quality · Micromorphology

1 Introduction

Technosols (IUSS Working Group WRB 2022) are "human-made soils", formed on, or containing technogenic materials. Their parent material can occur on any land surface affected by human activities (except agriculture). In some cases, a certain proportion (up to 20%) of technogenic materials and high levels of heavy metals, polymers, hydrocarbons, etc. can be produced in the soils (Alengebawy et al. 2021; Nachtergaele 2005). Mining activities result in large-scale landscape transformations as well as environmental pollution. Tailings are one of the areas of greatest concern as they constitute the Technosols' parent materials that have a great potential to release contaminant materials (Oliveira-Filho and Pereira 2023). Adrianto et al. (2023) suggest that extraction and mineral reduction produce around 8 Gt of tailings worldwide. In addition, hydrothermal activity, which results in the ore mineralization (i.e., the transformation of the host rocks) within mining regions, also has the potential to generate components that resemble pedogenic/weathering products such as clay minerals and fine particles of iron oxides and carbonates (Velde and Meunier 2008; Zhong

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et al. 2023). Therefore, the soil development on hydrothermally altered rocks proceeds faster than natural weathering. Such an accelerated pedogenesis is induced by a specific mechanism of secondary mineral accumulation. In most other soils, secondary components like clay minerals and iron oxi-hydroxides are produced by pedogenic chemical alteration of primary minerals, which is one of the slowest soil-forming processes with a characteristic time of about 10^4–10^6 years (Targulian and Krasilnikov 2007). However, in the case of pedogenesis on hydrothermal alterites, both clay and ferruginous components are already present in the parent material and can easily be released as a result of disintegration and, sometimes, also a partial dissolution of primary minerals of the host rocks (Sedov and Shoba 1996), Those processes develop much faster than neoformation and accumulation of pedogenic secondary minerals. This specific mechanism of release and accumulation of secondary minerals from hydrothermally altered rocks motivated Chernyakhovsky et al. (1976) to separate these rocks into a special class in their classification of weathering crusts. Even earlier, Kubiëna (1970) had already pointed out that "volcanothermic" processes could produce soil-like materials enriched in iron oxides and clay that could be easily confused with the lateritic products of long-term tropical weathering. The majority of 2:1 clay minerals within young volcanic tropical soils have a hydrothermal origin (Jongmans et al. 1994). In cool temperate regions with relatively low rates of weathering, pedogenesis on hydrothermally altered basic rocks generates soils with high contents of accumulated clay (Sedov et al. 1989). Such rocks can support specific "endemic" soil types, such as rubified smectitic Cambisols on the altered dolerites of Valaam island, which greatly differ from surrounding Podzols on crystalline rocks of the Baltic Shield (Sedov et al. 1993). Our earlier research within the arid subtropical region of Sonora has shown that a major part of clay material, especially smectites in the natural alluvial soils of Tinajas River (both surface and buried), is also derived from the hydrothermally altered andesites exposed in the area (Ibarra-Arzave et al. 2019). The valley of the Tinajas River is located quite close to the Buenavista del Cobre mining area, which suggested to us that hydrothermal geological materials containing clay could also be encountered among local mine wastes.

These general considerations as well as available data from regional observations on pedogenetic trends on hydrothermally altered rocks have led us to a hypothesis about the potential usefulness of such rocks for the construction of Technosols for mine site recultivation. In this respect, it is important to further observe the trends of early pedogenesis in the recent Technosols that incorporate hydrothermal materials. We have previously studied a short-term (decadal scale) chronosequence of Technosols on altered conglomerates within the tailings of the Peña Colorada iron ore mine (Díaz-Ortega et al. 2022). Those Technosols developed in well-drained positions under restored forest vegetation.

An efficient and environment-friendly approach to the remediation of mining areas is the creation of artificial wetlands, which is regarded as a passive technology. Artificial or man-made wetlands are characterized as water-saturated sediments processed by plants that can adapt to waterlogging conditions. Such plants play an important role in the retention of heavy metals, either through chelation with their organic compounds or bioaccumulation within their tissues, which helps wetlands to become more helps wetlands to restore their ecological function (Pat et al. 2018). Artificial wetlands have been successful because they contain limestones, clays, and organic compounds (such as manure, peat, and composts), i.e., the materials with the capacity to neutralize acidic solutions over very long periods, creating anoxic conditions to reduce the levels of sulfides present in the acid drainages (Skousen et al. 1998, 2017; US-EPA 2014). The main chemical reactions within artificial anoxic wetland systems include the reduction of Fe^{3+} to Fe^{2+} due to the absence of dissolved oxygen and the reduction of sulfides that induces the precipitation of pyrite with a respective change in pH. It is well-known that the presence of limestone increases the basicity of the aqueous medium and the rates of precipitation or coprecipitation of potentially toxic elements (López et al. 2004; Rivera-Uria et al. 2020). In order to create highly efficient artificial wetlands for tailing reclamation in arid climates, the water deficit problem can be solved with the use of wastewater.

This study was conducted within the Buenavista del Cobre copper mine located in Sonora State, Mexico. The study area is characterized by an arid climate; therefore, tailings have been treated with wastewater from the Cananea district. Consequently, the main objective of this work was to characterize the pedogenetic trends and the ecological quality of Technosols developed on the hydrothermal geological materials of mine tailings within artificial wetland ecosystems created with the use of wastewater.

2 Materials and methods

2.1 Geological and environmental characteristics of the study site

The Buenavista del Cobre mine is in the municipality of Cananea, North Sonora, México, which is dedicated to copper extraction (Fig. 1). The basement of the Cananea region consists of Precambrian metamorphic rocks (mainly schists) intruded by granitic rocks characterized by two magmatic facies: granitoids of quartz, K-feldspars and oligoclase, and granitoids of K-feldspar, oligoclase, quartz, hornblende, magnetite, and apatite (Valentine 1936). These Precambrian

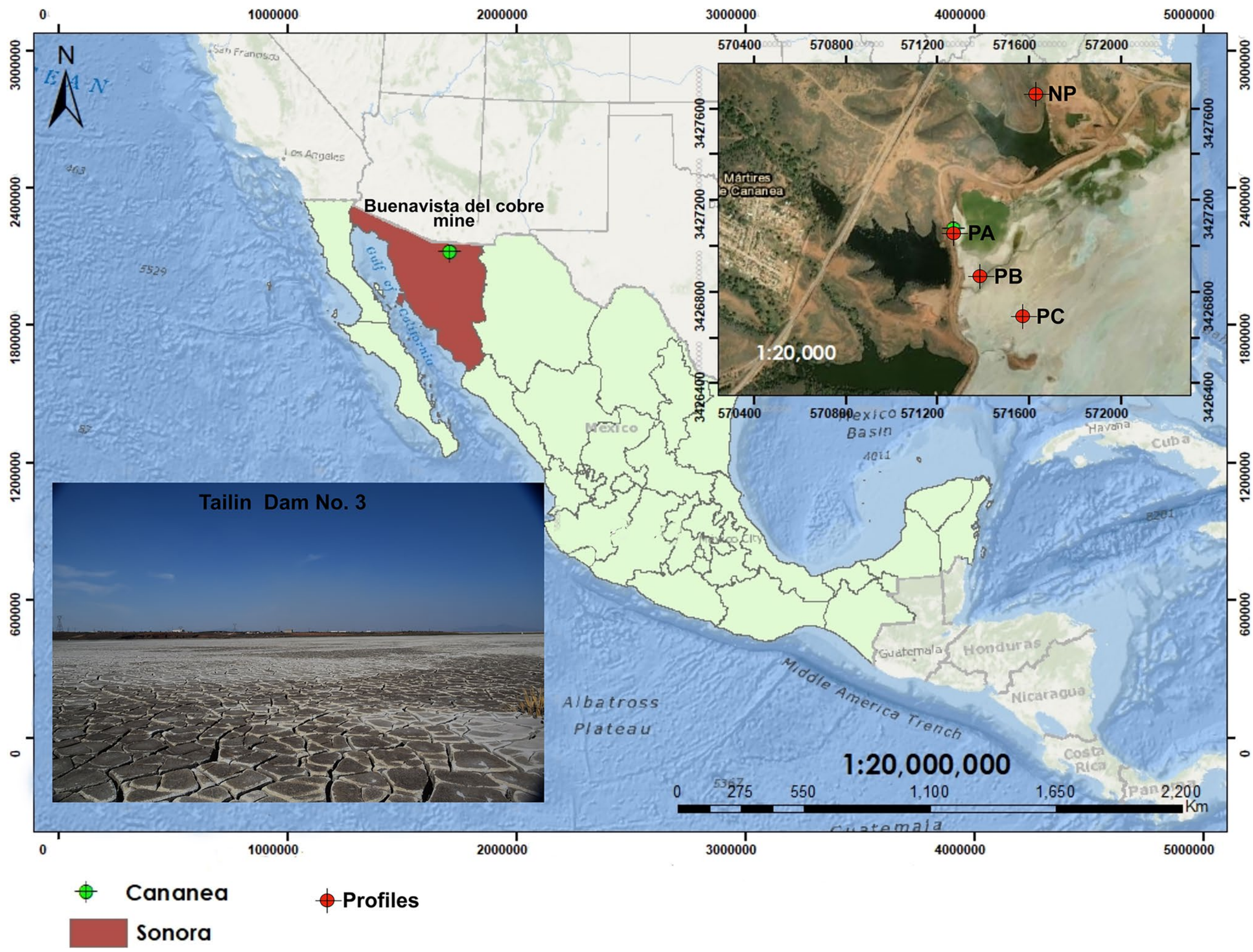


Fig. 1 Buenavista del Cobre mine location in NW Mexico. Location of the sampling points inside and around tailing dam number 3

rocks are covered by Paleozoic sedimentary calcareous rocks (Anderson and Silver 1979), which discordantly underlay Mesozoic volcanic rocks (Valentine 1936; Meinert 1982; Bushnell 1988). The open-air mining production is mainly associated with copper porphyries hosted by volcanic rocks. The lithological assemblage is formed by quartz-monzonite, monzodiorite, and granodiorite with sericite and skarns enriched with Zn-Pb-Cu (Ochoa-Landín et al. 2011). The age of the porphyry copper deposits is from the Late Cretaceous to the Eocene (Valencia-Moreno et al. 2007). Recent studies have shown that the productive rock has a porphyry texture composed of K-feldspar (40%), biotite (10%), plagioclase (10%), and quartz (30%) in a fine-grained matrix (Santillana-Villa et al. 2021). This kind of porphyry copper deposit is magmatic-hydrothermal. The rock is altered to sericite. Additionally, the strong hydrothermal alteration of the rocks has been geochemically characterized by the removal of Ca, Na, and K and the accumulation of Al (Santillana-Villa et al. 2021).

The climate within the region is semiarid, semi-hot, with a mean annual temperature of 18.5 °C and an annual precipitation of 545 mm, with rainfall maxima in July and August (INEGI 2017). The vegetation is dominated by xerophytic shrubs (*Thymophylla acerosa*, *Cyphomeris gypsophiloides*, *Mortonia scabrella*, *Quercus pungens*, *Flourensia*, and *Fouquieria splendens*), according to Van-Devender et al. (2010).

Mine tailings are characterized by high concentrations of Fe, Mn, Cu, and Zn; relatively lower concentrations of As, Cr, Cd, and Pb; pH values of around 4; and electric conductivity (EC) values of 3150 μS/cm (Reyes-Tenorio 2022). These characteristics are indicative of environmental problems associated with the mobilization of metals in the acidic medium. We selected for this study one of the mine tailing dams (number 3), which has an area of 2000 ha and is filled with wastewater coming from the city of Cananea. For decades, mine authorities have discharged wastewater due to the scarcity of water in the area (Fig. 1), The chemical and biological characteristics of the wastewater are presented in Table 1.

Table 1 Selected chemical properties of the wastewater of Cananea City

As	mg/L	0.042
Cd	mg/L	< 0.002
Cu	mg/L	0.059
Fecal coliforms	MPN/100 ml	7
Total coliforms	MPN/100 ml	1200
Electric conductivity	uS/cm	1450
Cr	mg/L	< 0.01
Biochemical oxygen demand	mg/L	32
P	mg/L	1.3
Fe	mg/L	2.68
Hg	mg/L	< 0.0005
Ni	mg/L	< 0.05
N	mg/L	8
pH		9.3
Pb	mg/L	0.019
Total dissolved solids	mg/L	1210
Total suspended solids	mg/L	192
SO_4^{2-}	mg/L	620
Zn	mg/L	0.053

MPN most probable number in 100 ml

2.2 Field survey and selection of profiles

Three sampling points were selected within the studied tailing dam depending on the degree of the wastewater influence: the PA profile under continuous waterlogging conditions; the PB profile under periodic conditions of saturation with wastewater; and the PC profile with no influence of wastewater. Additionally, a natural soil profile (NP) located outside of the mine tailing was sampled (Fig. 1). Descriptions were made following the guidelines of the FAO (2006). Bulk samples and undisturbed samples from every horizon were taken for laboratory analyses and micromorphological observations, respectively.

2.3 Micromorphology

Soil blocks with undisturbed structures were dehydrated at 40 °C for 3 days and impregnated with a polyester resin under vacuum at 24 micro-atmospheres. After impregnation and solidification, the blocks were cut, mounted on the cover glass, and cut again to make a 200-μm-thin section, which was finally polished to a thickness of 30 μm. Micromorphological observations were performed under an Olympus BX51 petrographic microscope equipped with a digital camera and Image Pro Plus 7.0 software. The descriptions were made following the Stoops (2003) terminology. Additionally, the overview book by Stoops et al. (2018) was used as a reference to identify soil-forming processes. Major attention was paid to the features of rapid pedogenetic processes that were expected to occur in the incipient syn-sedimentary Technosols, i.e., the development of structure and pore system (especially biogenic pores and aggregates) and the accumulation and transformation of organic materials. We analyzed granulometric and mineralogical characteristics of the soil mineral mass, with a special emphasis on the fine phyllosilicates of hydrothermal origin. We also recorded the abundance and morphology of the primary sulfide particles and looked for evidence of their oxidation.

2.4 Laboratory analyses

All the samples were dried in a drying oven at 40 °C and subsequently quartered and sieved through a 10-mesh to separate the < 2 mm.

The colors of dry samples were determined using Munsell color charts (2013). The pH and electrical conductivity values were determined in 1:1 (soil: distilled water) suspensions after shaking for 30 min at 200 rpm. The pH was measured with a Denver instrument Ultrabasic device calibrated with standard buffer solutions (the pH of 4, 7, and 10). The electrical conductivity was measured using an OAKTON CON 700 device calibrated with a 1413 μS/cm solution. Concentrations of As, Ba, Ca, Cu, Fe, Mn, Pb, Ti, V, and Zn were evaluated by X-ray fluorescence (XRF) using a Thermo Scientific Niton XL3t Ultra-portable analyzer in reading mode with three filters and an analysis time of 30 s. The equipment was calibrated with a standard blank using MONTANA 2710a, according to US-EPA 62000 (US-EPA 2007).

The soil fertility evaluation was based on analyzing the contents of organic matter, exchangeable bases (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}), and available P and nitrates ($N\text{-}NO_3$) in surface samples of all studied profiles using the following standard techniques: exchangeable bases by extraction with ammonium acetate (pH 7), available phosphorus by Bray 1 method, and nitrates using an ion-selective electrode. These analyses were performed in the "Fertilab" agricultural analysis laboratory (Mexico), certified by ISO 9001:2015 and accredited in both Mexico and the USA by the Intercomparison programs NAPT (North American Proficiency Testing), CAP (Compost Analysis Proficiency), MAGRUDER and SMCS, and according to NMX-EC-17025-IMNC-2018 Standard (ISO/IEC 17025:2017).

2.5 Clay mineralogy

Clay fractions were analyzed by the X-ray diffraction (XRD) method in three samples from the following locations: the unaltered tailing, the profile in the artificial wetland affected by wastewater, and the natural soil near the tailing. Clay fraction (< 2 μm) was separated by gravity sedimentation in distilled water from the samples dispersed with sodium pyrophosphate and then saturated with Mg. X-ray diffraction patterns were obtained using an EMPYREAN X-ray diffractometer operating at an accelerating voltage of 45 kV and a filament current of 40 mA, using CuKα radiation, nickel filter, and PIXcel 3D detector. Four oriented specimens on glass slides were prepared from each sample: air-dried (AD), saturated with ethylene glycol (EG), and after heating at 450 and 550 °C. Qualitative identifications of the most abundant clay minerals were based on the positions of basal diagnostic peaks and their modifications after glycolation and heating.

3 Results

3.1 Profile morphology

The PA profile (under continuous waterlogging conditions) is 30-cm thick (Fig. 2a, b). Its 0–1-cm layer consists of organic matter and a biofilm of algae. The AC horizon (0–10 cm) is dark gray (5Y 6/1), with abundant fine roots and a sandy clay loamy texture. It also has reddish-brown stains of iron oxides. The gray (5Y 6/1) Cur horizon (10-30 cm) has a silty clay texture, with few very fine roots. The water table is present at a depth of 18 cm. The plant species identified at the surface of this profile were as follows: *Populus fremontii* S. Watson, *Salix goddingii*, *Typha domingensis* Pers., and *Polypogon monspeliensis* (L). This profile was classified as Spolic Gleyic Technosol (Ochric), according to the WRB (2022).

The PB profile (with periodic waterlogging) is much thicker (80 cm), but it is entirely composed of grayish Cur horizons, labeled as Cur1 to Cur5 (Fig. 2c, d). The gray (5Y 6/1) Cur1 horizon (0–10 cm) has a silty clayey texture, yellowish-brown spots, and few medium-sized roots, with few fine vesicular pores. The Cur2 horizon (10–20 cm) is lighter in color (2.5Y 6/2) and is sandier and more compact, without any roots. Abundant pyrite was observed. The rest of the Cur3 horizons have similar colors (they are mainly gray), a silty clay texture, and a massive structure where thin laminations. *Salix goddingii* was the only plant species identified. This profile was classified as Hyperpolic Tidalic Technosol (Anoarenic, Orchric).

The PC profile (free of wastewater) has similarities with the PB profile in thickness, horizonation, and texture. Differences were also detected. At the profile surface, a 1-cm-thick yellowish-brown oxidized zone could be seen. The Cur horizon is massive with few fine roots; it tends to form desiccation polygons separated by 1 cm fractures (Fig. 2e, f). The Cur2 horizon (10–22 cm) is lighter (yellowish brown, 2.5Y 6/3). Spots were seen, possibly associated with differences in oxidation–reduction patterns. It is more porous and friable, without

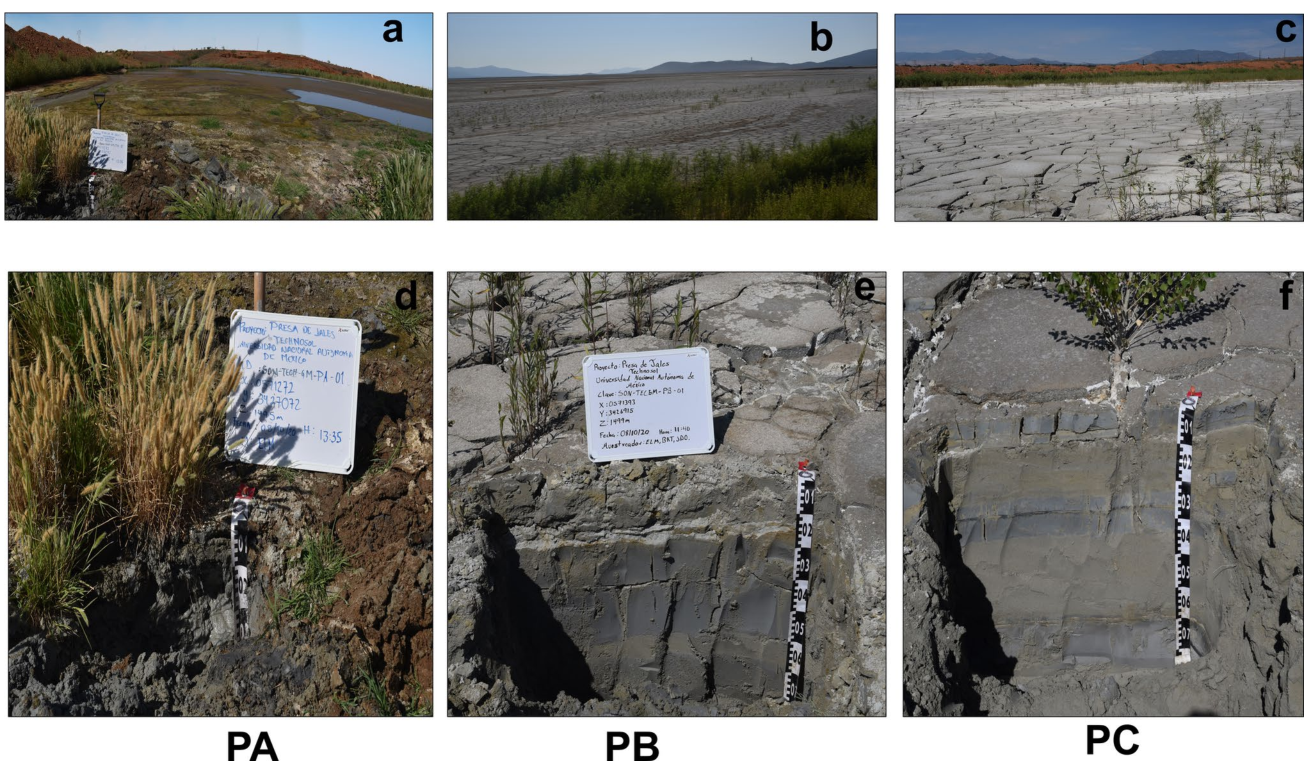


Fig. 2 Buenavista del Cobre tailing dam number 3. **a** Landscape of the wetland where the PA profile is found; **b** landscape of the transitional PB profile; **c** landscape of the dry area where the PC profile is found; **d** morphology of the PA profile; **e** morphology of the PB profile; and **f** morphology of the PC profile

any traces of roots, but with laminations. The Cur3 horizon (22–33 cm) is more compact and massive. It has stains and spots of oxidation. Cracks filled with sandy material from the upper horizon were observed. The Cur4 (33–60 cm) and Cur5 (60–73 cm) horizons are massive and friable, with abundant small vesicular pores. This profile was classified as Hyperspolic Gleyic Epistagnic Technosol (Ochric).

The NP profile (natural soil) had been sampled from a naturally drained position (Fig. 1), close to the dam. The profile consists of the following horizons (Fig. 3): AB (0–3 cm), Bw (3–20 cm), Btg (20–45 cm), and Bt (45–90 cm). The AB horizon is dark brown (7.5YR 3/4) with a silty loam texture, abundant fine and medium roots, and a high content (more than 25%) of rock fragments. The Bw horizon is more reddish (5YR ¾) and clayey, with abundant fine roots and a stoniness of up to 50%. The Btg horizon is more yellowish (5YR 4/6) and sandy, with few fine and medium roots and a higher percentage (around 70%) of rock fragments. The lowermost Bt horizon is more reddish (2.5 YR 4/6) containing dark-reddish stains of Fe and Mn oxy-hydroxides. In this horizon, the stoniness is close to 50%. A single plant species was identified as *Populus fremontii* S. Watson. This profile was classified as Amphistagnic Amphiskeletic Luvisol (Cutanic, Ochric), according to WRB (2022).

However, a much more detailed and diverse taxonomy of technogenic soils has recently been developed within the Polish Soil Classification, according to which the studied profiles on the tailings belong to Industriosols (Kabała et al. 2020).

3.2 Micromorphology

Micromorphological observations showed that the non-waterlogged profile (PC) had a compact arrangement of groundmass, without any large voids and channels or fissures, only with a few very small packing voids between coarse grains. The groundmass is dominated by silt-sized grains of feldspars and quartz. Small elongated particles of phyllosilicates are frequent. Fine material is pale and clayey, with a crystallitic b-fabric (due to abundant tiny sericite specks) (Fig. 4a). Primary sulfides are represented by black opaque grains of irregular and, less frequently, cubic shapes (Fig. 4b). We observed some areas with sharp boundaries strongly enriched with an orange-brown ferruginous pigment (Fig. 4c). Also, there are some areas with frequent black

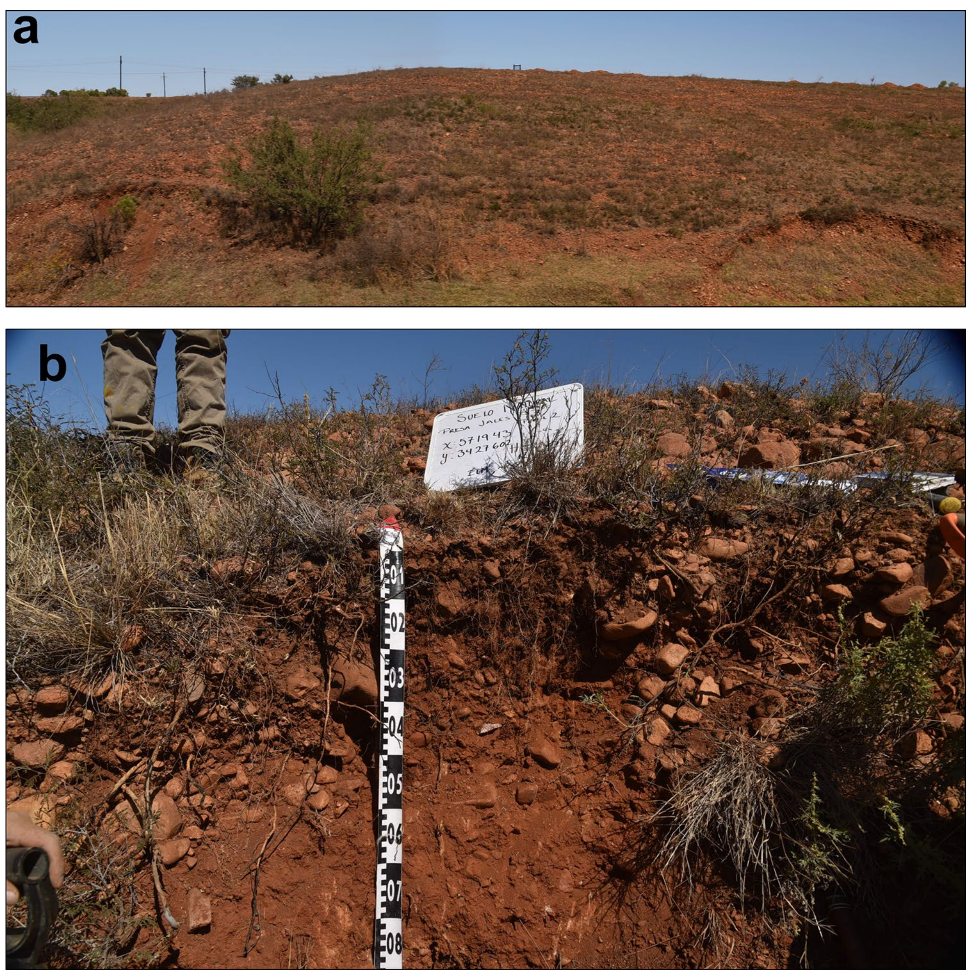


Fig. 3 Natural soil profile (NP). **a** Landscape of the natural profile and **b** morphology of the natural profile

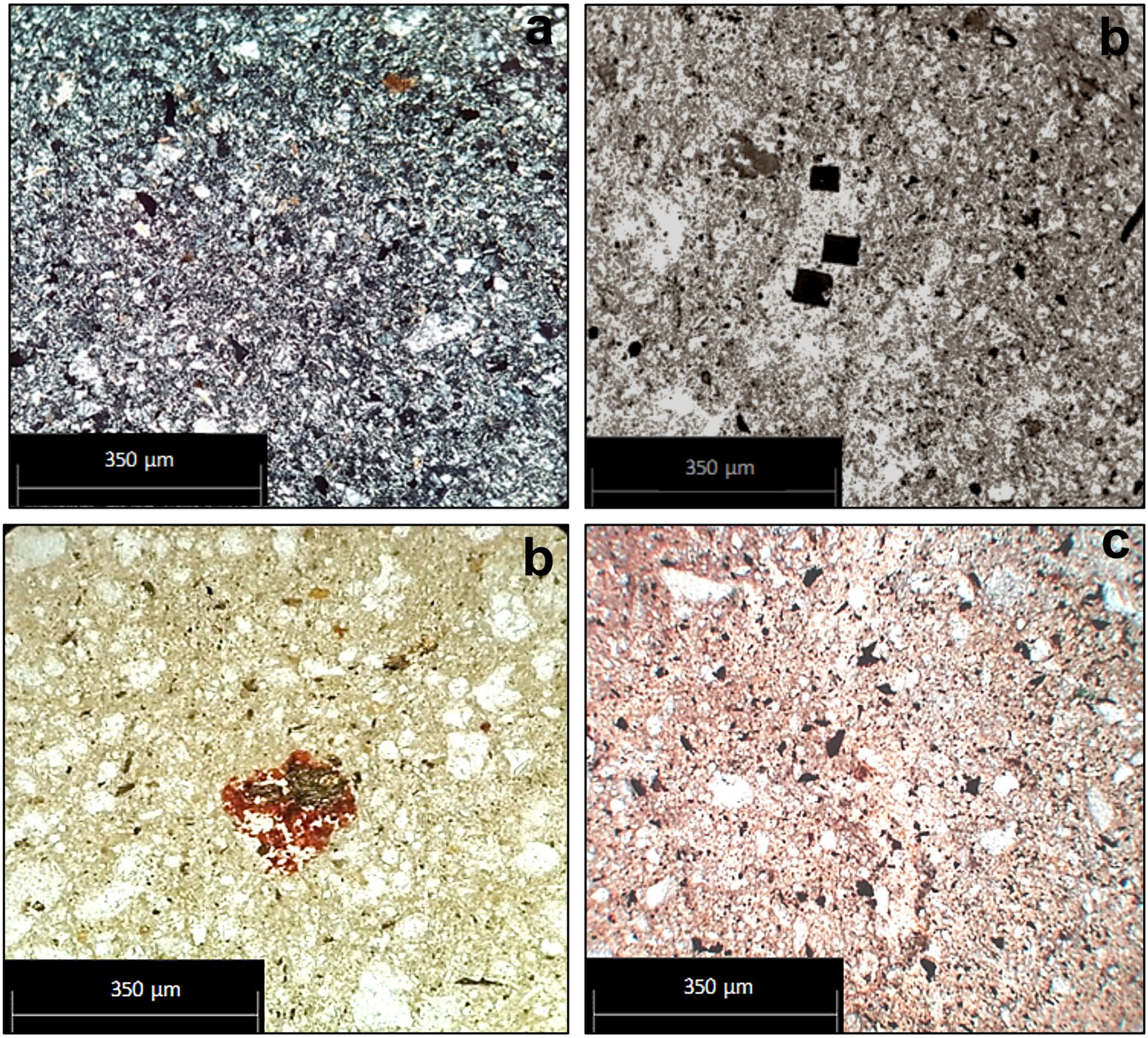


Fig. 4 Micromorphology of the PC profile, the Technosol on the tailings not treated with wastewater. **a** Compact groundmass, crystallitic b-fabric defined by sericite particles (N+). **b** Cubic crystals of fresh sulfidic minerals incorporated into the groundmass (PPL). **c** Area strongly impregnated with the ferruginous fine material (PPL). **d** Area with diffuse ferruginous pigmentation (left side of the view field) (PPL). PPL plain polarized light, N + under crossed polarizers

sulfidic particles that have a diffuse uneven ferruginous pigmentation (Fig. 4d). We suggest that these pigmented areas are indicative of the incipient oxidation of ferrous sulfides.

The most important distinction of the permanently waterlogged profile (PA) is the soil material re-organization at a micro-scale, which is due to biological agents. For example, there are numerous fresh roots that generate a set of large channel voids in the A horizon (Fig. 5a). We also observed the arrangement of mineral particles of different sizes around the roots, generating an incipient microstructure within some areas (Fig. 5b). A fine dark-brown organic material is produced at the periphery of some roots at the initial stage of decomposition (Fig. 5c). Very few small fresh roots were found even within the deeper C horizon (Fig. 5d), although a major part of its material was quite compact. However, we did not find any evidence of sulfide oxidation and generation of ferruginous fine material in this profile.

The periodically waterlogged profile (PB) has micromorphological similarities with both the permanently waterlogged and the completely dry profiles. On the one hand, it contains organic materials, fresh and degrading roots, as well as bio-channels generated by them. On the other hand,

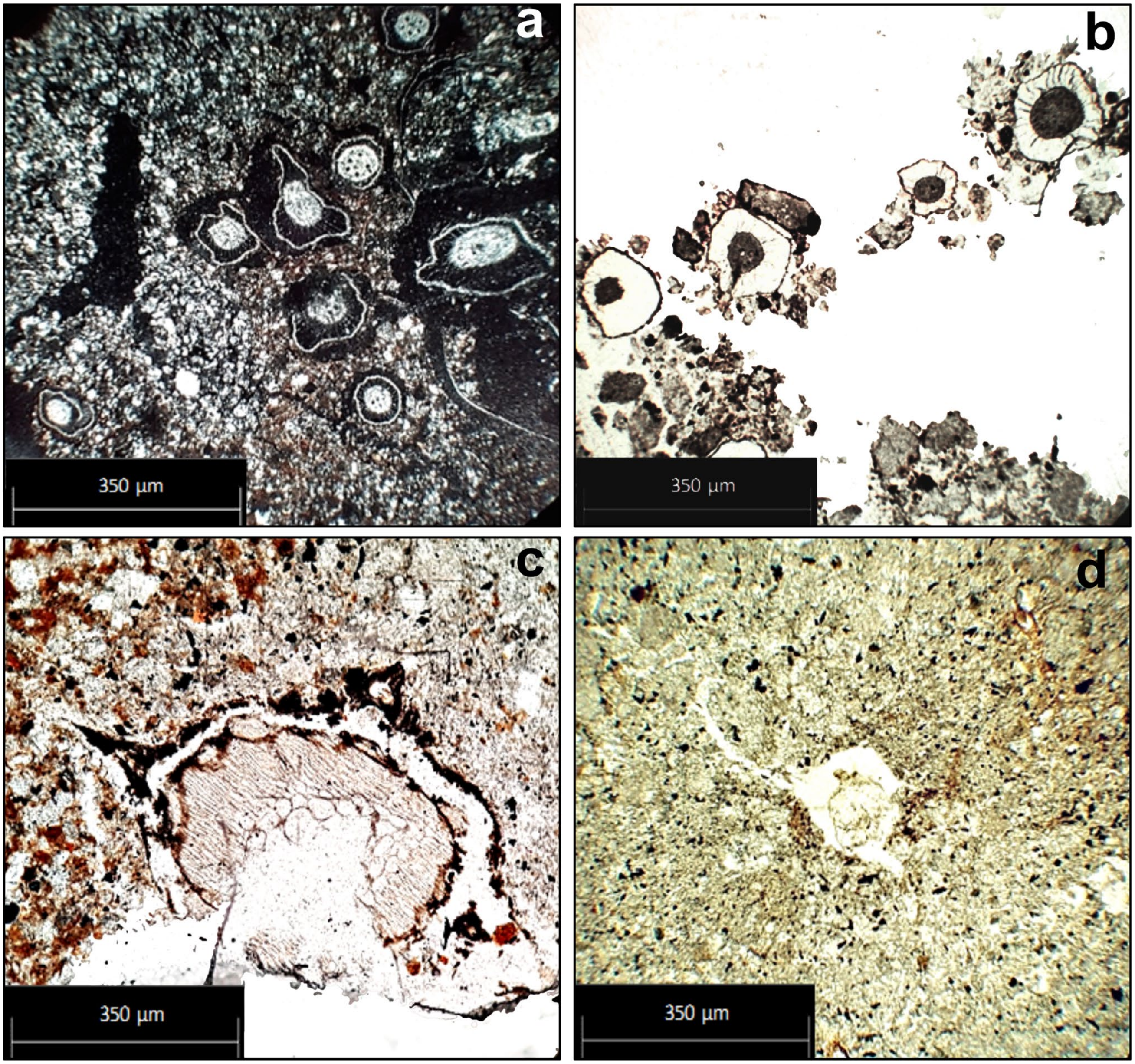


Fig. 5 Micromorphology of the PA profile, the hydromorphic Technosol on the tailings treated with wastewater. **a** Fresh root generating biogenic channel voids (N+). **b** Aggregation of groundmass components around the roots (PPL). **c** Dark brown humus pigmentation around decomposing root (PPL). **d** Single-root channel in the lower AC horizon (PPL). PPL plain polarized light, N+under crossed polarizers

it has signs of sulfide oxidation and some areas with a faint uneven ferruginous pigmentation.

The micromorphological pattern of the NP profile is completely different. Its groundmass is dominated by brown iron-clay fine material, in which isolated coarse grains of silicate minerals are immersed, giving rise to the porphyric coarse–fine related distribution. In the upper horizons, there are frequent signs of mesofauna activity, e.g., excremental infillings in the pores (Fig. 6a). Thick undisturbed clay coatings with high birefringence were encountered in the B horizon (Fig. 6b).

3.3 Chemical properties

The pH of the natural soil (NP profile) is acidic with values between 5.2 and 6.0. This soil has a low electric conductivity (EC values from 25.2 to 91.5 µS m^{-1}). The exchangeable cation concentrations and the CEC (cation exchange capacity) values are lower than those observed in the tailing profiles (Table 2). In contrast, the organic matter content is much higher in the A and Bw horizons, but the P and nitrate (N-NO^3) concentrations are lower. The profiles formed on

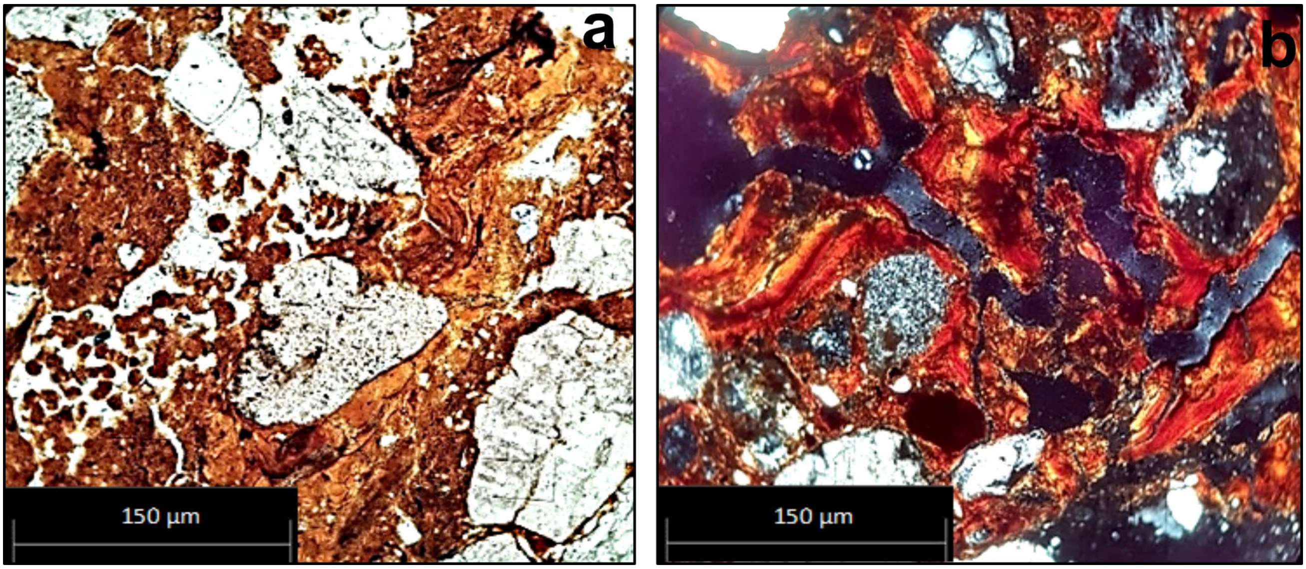


Fig. 6 Micromorphology of the NP profile, the natural background soil; **a** infilling of coprogenic granular aggregates in a large pore (PPL). **b** Clay coatings with strong interference colors (N+). PPL plain polarized light, N+under crossed polarizers

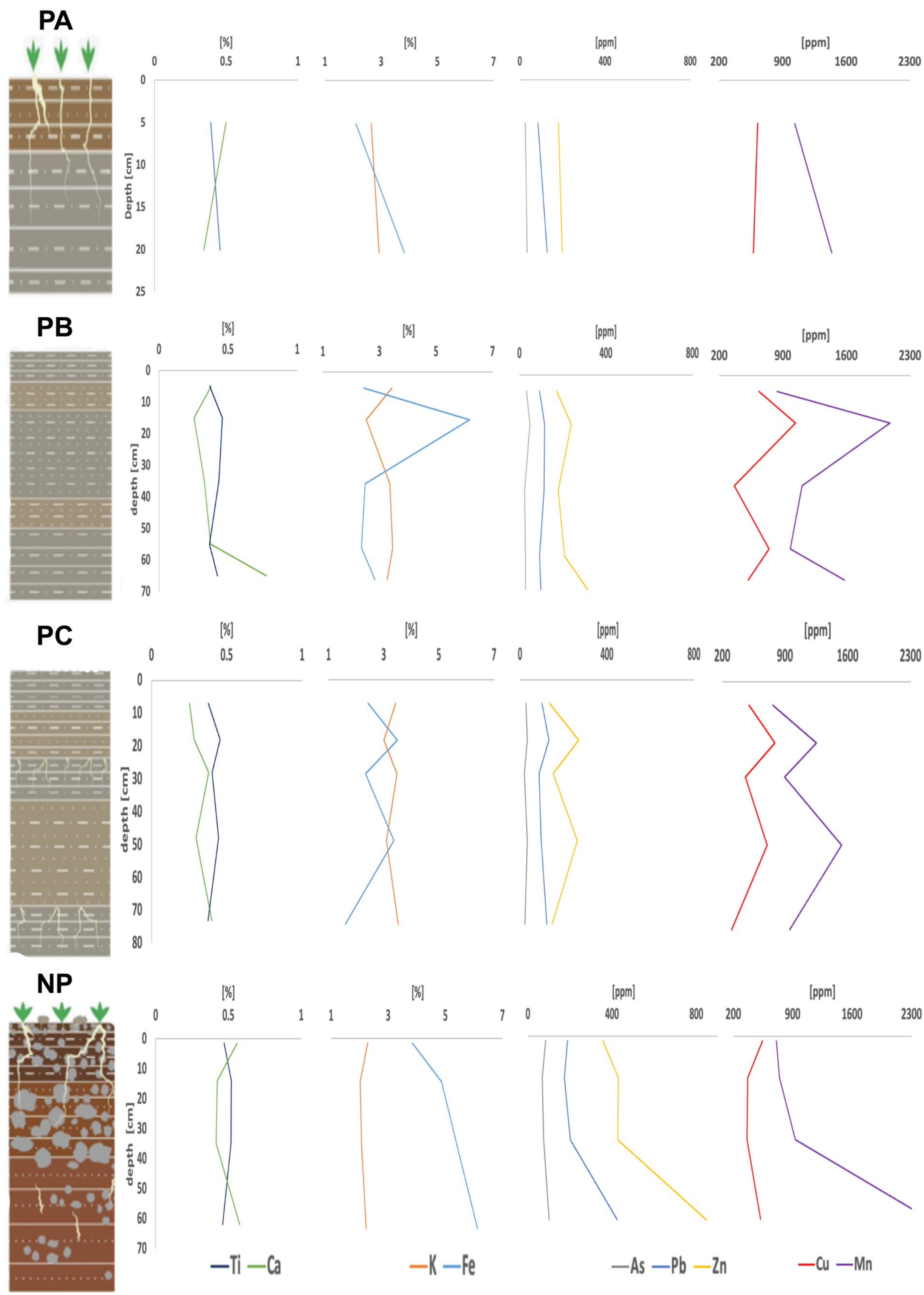
the mine tailing have neutral to slightly alkaline pH and high EC values. Relatively higher pH values were detected in the PA profile, while the highest EC value (2140 μS m^{-1}) was found in the Cur1 horizon of the PB profile together with the highest concentrations of exchangeable cations (Table 2). All three soil profiles have concentrations of organic matter below 0.35%. The highest phosphorus contents of 102 and 110 ppm were observed in the lowermost horizons of the PA and PC profiles, respectively. The content of nitrates is very low in the studied profiles.

Table 2 Selected chemical properties of the studied soils

Profile	Horizon	Depth (cm)	pH	EC (μS m^{-1})	Exchangeable cations ($cmol_c$/kg)				CEC ($cmol_c$/kg)	OM (%)	P (ppm)	N-NO_3 (ppm)
					Ca	Mg	K	Na				
PA	AC	0–10	7.9	948.0	10.70	0.94	0.16	0.36	12.2	0.31	63.0	0.20
	Cur	10–30	7.5	432.0	6.28	0.48	0.07	0.12	7.0	0.15	102.0	0.10
PB	Cur1	0–10	6.8	2140.0	23.1	1.46	0.74	3.2	28	0.27	48.0	0.02
	Cur2	10–20	6.2	428.0	3.68	0.29	0.07	0.1	4.6	0.25	54.8	0.02
	Cur3	20–50	6.4	593.0	11.3	0.44	0.27	0.2	12.2	0.33	32.0	0.01
	Cur4	50–60	6.7	276.0	6.31	0.13	0.13	0.11	6.7	0.13	30.0	0.02
	Cur5	60–85	6.9	637.0	13.3	0.27	0.23	0.16	14.0	0.25	31.0	0.02
PC	Cur1	0–10	6.8	962.0	9.52	0.44	0.74	1.05	11.8	0.33	47.0	0.20
	Cur2	10–22	6.9	533.0	7.81	0.19	0.17	0.12	8.3	0.35	98.0	0.20
	Cur3	22–33	7.1	754.0	8.91	0.27	0.15	0.13	9.5	0.13	25.0	0.20
	Cur4	33–60	7.3	352.0	5.91	0.18	0.19	0.14	6.4	0.28	27.0	0.20
	Cur5	60–73	7.3	726.0	9.42	0.26	0.29	0.2	10.2	0.26	110.0	0.20
NP	AB	0–3	5.3	91.5	4.99	0.97	0.47	0.07	7.0	4.58	19.0	19.0
	Bw	3–20	5.2	36.4	6.02	1.21	0.44	0.04	7.8	2.60	7.13	5.0
	Btg	20–45	5.5	30.8	ND	ND	ND	ND	ND	ND	ND	ND
	Bt	45–90	6.1	25.2	ND	ND	ND	ND	ND	ND	ND	ND

ND no determinate

[a] Available phosphorous


PA
PB
PC
NP
Depth [cm]
depth [cm]
[%]
[ppm]
Ti
Ca
K
Fe
As
Pb
Zn
Cu
Mn

◂**Fig. 7** Bulk chemical composition (total Ti, Ca, K, Fe, As, Pb, Zn, Cu, and Mn) of the studied profiles. PA hydromorphic Technosol, PB periodic waterlogging conditions, PC not irrigated with wastewater

3.4 Bulk chemical composition

The proportions of total Ti and Ca only insignificantly differ and tend to be below 0.6% in all studied profiles. However, there is a small increase in the Ca content within the lowermost parts of the PB and NP profiles (Fig. 7). The K contents are similar in all tailing profiles but higher in the NP profile. Interestingly, the NP has significantly higher concentrations of As, Pb, and Zn as compared to those measured in the PA, PB, and PC profiles. The Cu contents show clear differences between the studied profiles, being relatively higher (between 300 and 1038 ppm) in the profiles associated with the tailings dam. Finally, the Mn values are very variable between the profiles, i.e., above 1000 ppm in the PA profile and from 836 to 2079 ppm in the PB profile. The same tendency was observed in the PC and NP profiles, with the Mn values between 763 to 1528 ppm and 745 to 2505 ppm, respectively.

3.5 Clay mineralogy

The diffractograms of the clay fractions of the three studied samples (C horizon of the Technosol with no wastewater, artificial wetland Technosol, and natural soil) show striking similarities in their clay mineral composition (Fig. 8). All three samples contain predominantly two minerals, as indicated by their very strong first basal maxima: illite (peak at 1.0 nm, not changing upon pre-treatments) and kaolinite (peak at 0.7 nm that collapses after heating at 550 °C). However, some differences were also detected, such as some small modifications of those major maxima and the presence of small additional peaks indicative of minor clay components. The diffractogram of the sample from the untreated Technosol has a small additional peak at 1.4 nm; it stays unchanged for all pretreatments. This peak is indicative of chlorite. In this case, the tiny peak at 0.7 nm, being left after the collapse of the high 0.7 nm maximum upon heating at 550 °C, is the second-order maximum of chlorite. In the waterlogged Technosol, the behavior of the minor 1.4-nm peak is different. After the pretreatment with ethylene glycol, a part of this maximum moves toward smaller angles and produces a new peak at 1.7 nm. After heating at 550 °C, the 1.4-nm peak also lowers, with a simultaneous rise of the 1.0 nm maximum. We conclude that a part of the 1.4-nm peak belongs to smectite, which shrinks to 1.7 nm after the adsorption of ethylene-glycol and shrinks to 1.0 nm upon heating. Diffractogram from the natural soil has the same major peaks at 1.0 nm and 0.7 nm; however, they are broader. The minor peak at 1.4 nm is also present and predominantly belongs to chlorite.

4 Discussion

4.1 Initial soil forming processes in the hydromorphic Technosols

One of the main considerations in studies of Technosols is to establish the rates of pedogenetic processes that transform human-made parent materials into environmentally suitable soils capable of providing ecosystem services (Huot et al. 2013; Santini and Fey 2016; Ruiz et al. 2020a; Queiroz et al. 2022; Weil and Brady 2016). Recent studies have demonstrated that tailing dams, due to their geochemical, mineralogical, and physical characteristics, can accelerate pedogenesis (Uzarowicz and Skiba 2011; Santini and Fey 2016; Ruiz et al. 2020b; Uzarowics et al. 2020).

The Technosols of Buenavista del Cobre have features indicative of the rapid development of soil-forming processes of a biogenic nature. Our microscopic observations revealed the development of incipient structure and porosity related to root growth. The accumulation of organic materials, especially fresh plant fragments and roots, was also observed. Such accumulation is not reflected in the measured organic carbon content, which remains low. We think that this is due to the size of the observed plant fragments; they are often larger than 2 mm, whereas the carbon measurements were performed in samples of fine earth that passed through the 2-mm sieve.

An important impact of hydromorphic conditions caused by wastewater inputs was the strong hampering effect of sulfide oxidation in the wetland Technosol. In thin sections from the untreated profile, we encountered a local pigmentation with the neoformed ferruginous fine material, which is the most common indicator of sulfide oxidation (Rivera-Uria et al. 2019). Only very few such features were present in the hydromorphic Technosol treated with wastewater. On the contrary, we observed frequent unaltered particles of primary sulfides retaining their original crystal shape. We conclude that the saturation with wastewater generates an anoxic regime that is additionally supported by the presence of dissolved organic matter. These conditions prevent the oxidation of pyrite and other primary sulfides and preserve them fresh and intact in the Technosols of the artificial wetland, whereas in the non-irrigated area of the tailing, the oxidation (although still incipient) has already started.

We further speculate that these differences in the weathering status of primary sulfide particles have important implications for the soil reaction. The pH values in the hydromorphic Technosols irrigated with wastewater are higher than those in all other studied profiles including transitional and non-irrigated parts of the tailing and the natural landscape. We explain the acidification of the non-irrigated soils by the above-described sulfide oxidation, which generates sulfuric

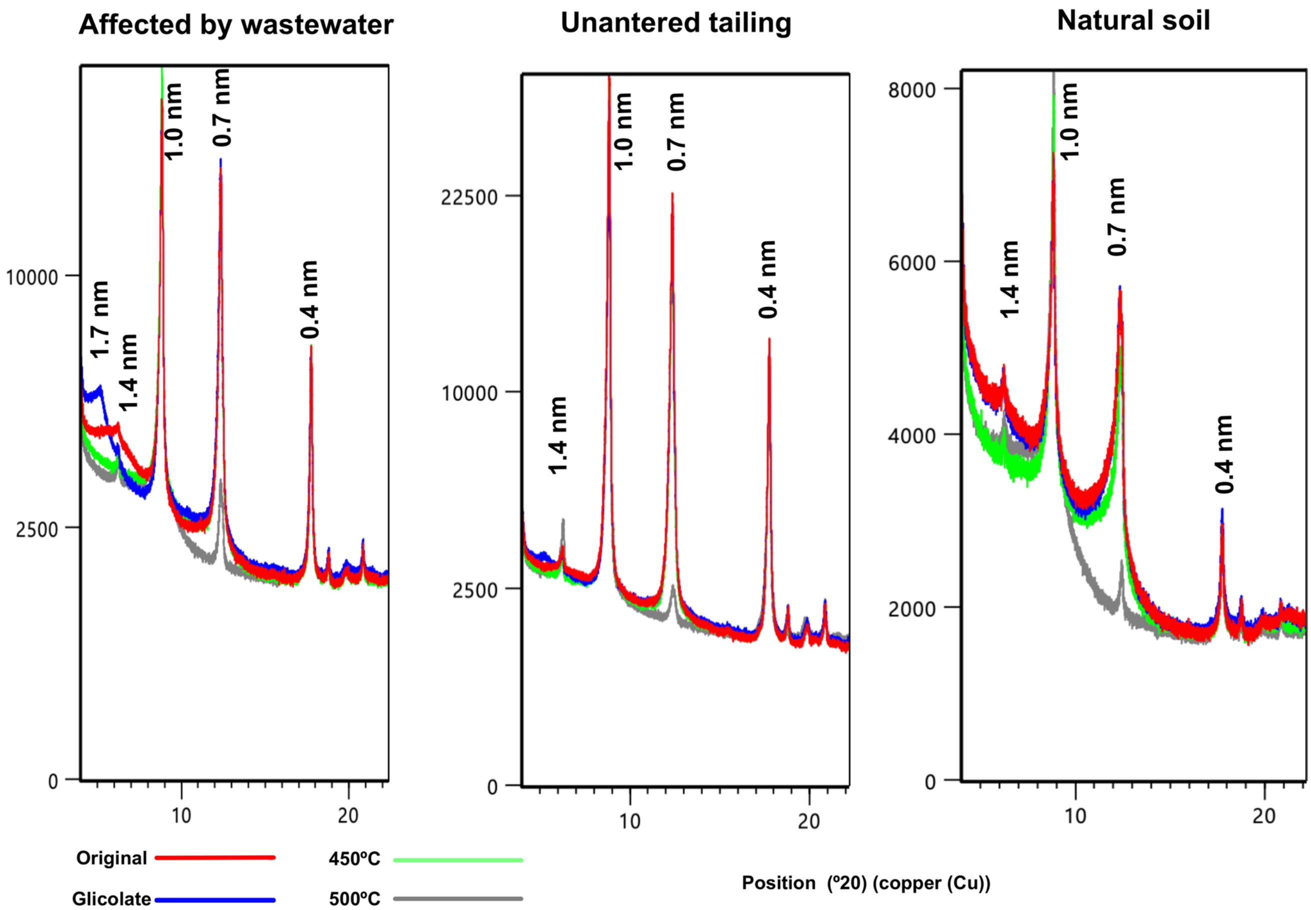


Fig. 8 Diffractograms of three selected samples: one affected by wastewater; unaltered tailing; and natural soil

acid. As the oxidation process is still at its initial stage, the current lowering of pH is modest.

Soil acidity controlled by primary sulfide oxidation is expected to influence the behavior of potentially toxic heavy metals. As stated above, some of them show relatively high bulk contents in the tailing sediment. However, a recent preliminary study has shown that the concentrations of pollutants (in particular Ag, As, Ba, Cd, Cr, Pb, and Se) extracted from the tailing substrate with water saturated with CO_2 are below the detection limits of the ICP method (Reyes-Tenorio 2022). Therefore, these metals are still retained within the structure of the host primary minerals and are not available for migration in the soluble form. Nonetheless, the signs of the incipient sulfide oxidation and the decrease in pH in the soils of the non-irrigated part of the tailings are warning us that in the future, with the progress of oxidation and acidification, the mobility of heavy metal contaminants could dramatically increase. In this respect, our results from the hydromorphic Technosols show that irrigation with wastewater and the creation of artificial wetlands are efficient approaches to curb these negative tendencies and thus avoid contamination of surrounding landscapes and ecosystems.

A further beneficial effect of wastewater inputs is the increase in available phosphorus observed in the hydromorphic profile. Nevertheless, salinity can be a problem as the EC is high.

4.2 Hydrothermal clay minerals in the Technosol and their influence on pedogenetic properties and trends

Some specific properties of the studied hydromorphic Technosol are related to the pre-pedogenic hydrothermal transformation of its parent material—a tailing deposit derived from the pulverized volcanic rock from the mine. The high content of fine material composed predominantly of phyllosilicates, in particular, sericite (very fine, partly hydrated mica of muscovite type), is observed in thin sections. We identified illite as a major component of the clay mineral assemblage revealed by X-ray diffraction (Fig. 8), which agreed with our microscopic observations and published data pointing to the abundance of sericite. We further speculate that highly crystalline kaolinite is also of hydrothermal origin and not a pedogenetic or weathering product. Soils and weathering mantles within the study area are only moderately developed in agreement with the semiarid to arid climatic conditions and do not reach the ferrallitic stage, which is necessary for large-scale kaolinite accumulation. However, kaolinite is quite a typical mineral formed during hydrothermal argillization, and it frequently accompanies sericite as a product of the metasomatic transformation of feldspars (Pirajno 2009). Chlorite also belongs to the hydrothermal association of phyllosilicates. Among the detected clay minerals, we suspect that smectite in the wetland Technosol on the tailing treated with wastewater could be of pedogenic origin, i.e., a product of chlorite transformation. The transformation of chlorite into vermiculite and smectite is usual in soil systems (Barnhisel and Bertsch 1989) and could readily occur in poorly drained environments (Ross et al. 1982). However, smectites could also be formed during hydrothermal alteration (Pirajno 2009). The hydrothermal origin of smectites in the alluvial soils near Cananea has earlier been confirmed by Ibarra-Arzave et al. (2019). In general, there is now a doubt whether most clay minerals in the studied Technosols have a hydrothermal origin or are the products of weathering. Surprisingly, there is very little difference between the composition of clay minerals in the studied Technosol and the background modern soils, despite the contrasting difference in their types of pedogenesis and grades of development. It means that the clay mineral assemblage, even in the much more developed natural profile, is dominated by the inherited hydrothermal components with a minor role in pedogenic transformation.

The abundance of hydrothermal silicate clay had a clear impact on various soil properties and features important for the biological soil quality. As the content of organic matter is low in the Technosol, silicate clay is responsible for the relatively high values of cation exchange capacity, which are similar to or even higher than those in the natural soil. This promotes the adsorption of nutrients in the cationic form, in particular, potassium. In addition, the cation exchange positions of clay minerals also generate possibilities for the retention of heavy metal cations. In the soils contaminated during the catastrophic spillage in Cananea, the sorption of clay minerals was especially important for the retention of copper (Romero-Lázaro et al. 2019). Finally, clay components play a fundamental role in the organo-mineral interactions and stabilization of humus in soil systems (Kleber et al. 2021). In the studied hydromorphic Technosol, organic materials are present predominantly in the form of living roots and fresh plant residues. However, our micromorphological observations showed that the formation of fine, dark organic colloidal materials was associated with the decomposition of organic tissues. We suppose that these materials have formed due to the interaction of organic compounds and clay minerals and that they are the first steps toward the accumulation of clay-humus fine material, which is a key component providing for a high physical and chemical quality of soils.

Recently, Díaz-Ortega et al. (2022) documented a fast pedogenesis in Technosols on tailings from an iron mine in Peña Colorada, Mexico. The rapid transformation is favored by the presence of hydrothermal components, mainly clay minerals, coming from the surrounding geological formations. In this way, Technosols emulate the natural pedogenesis of the area.

In general, the obtained results show that the incorporation of hydrothermally altered materials has a beneficial effect on the development of Technosols under hydromorphic conditions of artificial wetlands. The same effect has also been reported within well-drained mine site environments (Díaz Ortega et al. 2022).

5 Conclusions

Irrigation of tailings of the Buenavista del Cobre mine with the wastewater supported biological processes, including the development of plant root systems and a primary aggregation of the soil matrix, and enhanced the overall ecological soil quality of the hydromorphic Technosols developed in the artificial wetlands.

Saturation with wastewater containing dissolved organic matter and generating anoxic conditions strongly limits the oxidation of primary sulfides, which retain their unaltered crystalline morphology in the hydromorphic Technosols. Consequently, they have higher pH values that prevent the mobilization of heavy metals, despite their elevated bulk concentrations. In contrast, the material of non-irrigated areas of tailings shows evidence of incipient sulfide oxidation and acidification, which in the future could promote mobilization and migration of pollutants.

Technosols of the Buenavista del Cobre mine are rich in clay minerals, predominantly kaolinite and illite, which have a hydrothermal origin and are inherited from the pulverized rock of the tailings.

Clay minerals have a beneficial effect on the development of pedogenetic properties and processes, i.e., they provide for a high cation exchange capacity, which is important for nutrient storage, and produce organo-mineral compounds that favor the soil structure development. Hydrothermal clay minerals seem to be quite stable in the soil environment and show only a minor transformation even in the natural profiles.

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Declarations

Conflict of interest The authors declare no competing interests. All authors of this manuscript made substantial contributions to the research and qualify for authorship, and no authors have been omitted. We warrant that all the authors have agreed to this submission.

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