Szkoła Główna Gospodarstwa Wiejskiego

w Warszawie

Instytut Rolnictwa

mgr inż. Magdalena Barbara Tarnawczyk

Mineralogiczne, mikromorfologiczne i geochemiczne wskaźniki genezy i stopnia zanieczyszczenia gleb technogenicznych (Technosols) ukształtowanych w obszarach historycznego górnictwa i hutnictwa w Tatrach

Mineralogical, micromorphological, and geochemical indicators of genesis and pollution degree of technogenic soils (Technosols) developed on historical mining and metallurgical sites in the Tatra Mountains

Rozprawa doktorska

Doctoral thesis

Rozprawa doktorska wykonana pod kierunkiem
dr. hab. Łukasza Uzarowicza, prof. SGGW
Katedra Gleboznawstwa, Instytut Rolnictwa

Promotor pomocniczy
dr inż. Wojciech Kwasowski
Katedra Gleboznawstwa, Instytut Rolnictwa

Warszawa 2025

Oświadczenie promotora rozprawy doktorskiej
przygotowanej przez doktoranta Szkoły Doktorskiej SGGW

Oświadczam, że **rozprawa doktorska autorstwa Magdaleny Tarnawczyk została przygotowana pod moim kierunkiem na podstawie badań realizowanych w ramach kształcenia w Szkole Doktorskiej SGGW** i stwierdzam, że spełnia warunki do przedstawienia jej w postępowaniu o nadanie stopnia naukowego doktora.

Data 30.09.2025 Czytelny podpis promotora .....

Oświadczenie autora rozprawy doktorskiej
będącego doktorantem Szkoły Doktorskiej SGGW

Świadoma odpowiedzialności prawnej, w tym odpowiedzialności karnej za złożenie fałszywego oświadczenia, oświadczam, że **niniejsza rozprawa doktorska została przygotowana przeze mnie samodzielnie na podstawie badań realizowanych w ramach kształcenia w Szkole Doktorskiej SGGW** i nie zawiera treści uzyskanych w sposób niezgodny z obowiązującymi przepisami prawa, w szczególności z ustawą z dnia 4 lutego 1994 r. o prawie autorskim i prawach pokrewnych (tj. z dnia 28 października 2022 r., Dz.U. z 2022 r. poz. 2509 ze zm.)
Oświadczam, że przedstawiona rozprawa nie była wcześniej podstawą żadnej procedury związanej z uzyskaniem stopnia naukowego doktora.

Oświadczam ponadto, że niniejsza wersja rozprawy jest identyczna z załączoną wersją elektroniczną.

Przyjmuję do wiadomości, że rozprawa doktorska poddana zostanie procedurze antyplagiatowej.

Data 30.09.2025 Czytelny podpis autora rozprawy Magdalena Tarnawczyk

Niniejsze badania zostały sfinansowane ze środków Narodowego Centrum Nauki, projekt nr 2021/41/N/ST10/03129 (PRELUDIUM-20).

Spis treści

Wykaz publikacji wchodzących w skład rozprawy doktorskiej

Artykuł 1: **Tarnawczyk M.**, Uzarowicz Ł., Kwasowski W., Górka-Kostrubiec B., Pędziwiatr A., 2025. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena 247, 108521. https://doi.org/10.1016/j.catena.2024.108521

(MNiSW: 140 pkt; IF: 5.7)

Artykuł 2: **Tarnawczyk M.**, Uzarowicz Ł., Pędziwiatr A., Kwasowski W., 2025. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. Soil Science Annual 76(3), 211370. https://doi.org/10.37501/soilsa/211370

(MNiSW: 70 pkt; IF: 1.0)

Artykuł 3: **Tarnawczyk M.**, Uzarowicz Ł., Kwasowski W., Pędziwiatr A., Martín-Peinado F.J., 2025. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. Minerals 15(9), 988. https://doi.org/10.3390/min15090988

(MNiSW: 100 pkt; IF: 2.2)

Lista skrótów używanych w rozprawie

Al_{ox} – formy amorficzne i słabo krystaliczne glinu

BS – Nasycenie zasadowe (base saturation)

CEC – Pojemność kompleksu sorpcyjnego (cation exchange capacity)

EA – Kwasowość wymienna (exchangeable acidity)

EB – Wymienne kationy zasadowe (exchangeable bases)

F – Frakcja

Fe_c – krystaliczne tlenki żelaza pedogenicznego (crystalline pedogenic iron oxides)

Fe_d – wolne tlenki żelaza (free iron oxides)

Fe_{nf} – zawartość żelaza w postaci innej niż wolne tlenki

Fe_t – całkowita zawartość żelaza (total iron content)

F_{ox} – formy amorficzne i słabo krystaliczne żelaza

ICP-MS – Inductively coupled plasma-mass spectroscopy

ICP-OE – Inductively coupled plasma-optical emission spectrometry

Mnox – formy amorficzne i słabo krystaliczne manganu

P – Profil

PTTE – Potencjalnie toksyczne pierwiastki śladowe (potentially toxic trace elements)

REE – Pierwiastki ziem rzadkich (rare earth elements)

SEM-EDS – Scanning electron microscope – energy dispersive X-ray spectroscopy

Si_{ox} – formy amorficzne i słabo krystaliczne krzemu

SOM – Glebowa materia organiczna (soil organic matter)

TN – Azot całkowity (total nitrogen)

TPN – Tatrzański Park Narodowy

TOC – Całkowity węgiel organiczny (total organic carbon)

TS – Siarka całkowita (total sulphur)

Streszczenie

Tatry to wyjątkowy ekosystem alpejski w Europie Środkowej, gdzie dobrze rozpoznane są gleby naturalne i procesy glebotwórcze je kształtujące. Jednak gleby technogeniczne (Technosols) w środowisku wysokogórskim tego obszaru nie zostały dotychczas szczegółowo zbadane. Celem niniejszej rozprawy jest określenie najważniejszych czynników glebotwórczych kontrolujących właściwości gleb, a także zbadanie cech mineralogicznych, mikromorfologicznych i geochemicznych gleb technogenicznych w rejonach historycznego górnictwa i hutnictwa w polskich Tatrach dla rozpoznania stopnia zaawansowania procesów glebotwórczych i stopnia zanieczyszczenia tych gleb. Przeanalizowano trzynaście profili glebowych, podzielonych na trzy grupy: (I) gleby technogeniczne powstałe z odpadów górniczych stanowiących skały węglanowe (wapienie i dolomity) zawierające resztki rud żelaza i manganu, (II) gleby technogeniczne powstałe z odpadów górniczych pochodzących ze skał magmowych i metamorficznych (granit, gnejs) zawierających pozostałości rud polimetalicznych oraz (III) gleby technogeniczne zawierające odpady pochodzące z działalności hutniczej (np. żużle). Badania obejmowały określenie morfologii i klasyfikacji gleb, podstawowych właściwości gleb, podatności magnetycznej, składu mineralnego, cech mikromorfologicznych i submikromorfologicznych, pedogenicznych form Fe, Al, Si i Mn , a także całkowitej zawartości pierwiastków głównych, zawartości pierwiastków śladowych i ich form, a także zawartości pierwiastków ziem rzadkich.

Badane gleby technogeniczne były słabo ukształtowanymi glebami o prostej morfologii profilu glebowego (głównie poziomy O, A i C), z wysoką zawartością części szkieletowych. Badania wykazały, że właściwości gleb technogenicznych w Tatrach były determinowane przede wszystkim przez dawną działalność przemysłową człowieka, taką jak górnictwo i hutnictwo, a także rodzaj antropogenicznego materiału macierzystego (odpady górnicze i żużle hutnicze), który determinował właściwości gleby wraz z jej składem mineralnym i chemicznym. Na przebieg procesów glebotwórczych znaczący wpływ miała roślinność, której występowanie było uwarunkowane rzeźbą terenu i warunkami klimatycznymi zależnymi od piętra klimatyczno-roślinnego. Roślinność i pochodząca z roślin glebowa materia organiczna kształtowały właściwości wierzchniej warstwy gleby. Proces glebotwórczy trwający od kilku stuleci w niektórych glebach doprowadził do powstania poziomów Bw.

Analiza płytek cienkich z gleb ujawniła następujące mikromorfologiczne przejawy procesów glebotwórczych: (1) tworzenie się pseudomorfoz tlenku żelaza w wyniku wietrzenia siarczków; (2) tworzenie się pedogenicznej struktury w poziomach powierzchniowych; (3) tworzenie się pedogenicznych otoczek węglanowych w glebach powstałych z odpadów górniczych złożonych ze skał węglanowych; (4) tworzenie się pedogenicznych otoczek tlenków Fe i Mn w kwaśnych glebach powstałych z odpadów górniczych złożonych ze skał krystalicznych (granit, gnejs); (5) tworzenie się pedogenicznych otoczek siarczanowych w glebach zawierających żużle hutnicze

oraz (6) bioturbacje (np. kanały korzeniowe i kanały biogeniczne wypełnione materiałem przetworzonym przez zwierzęta glebowe). Obserwacje mikromorfologiczne wykazały również, że żużle hutnicze w glebach technogenicznych mogą stanowić siedlisko dla fauny glebowej (najprawdopodobniej nicieni lub wazonkowców). Selektywne ekstrakcje pedogenicznych Fe, Al, Mn i Si wykazały (1) uwalnianie Mn ekstrahowanego za pomocą szczawianu amonu w glebach powstałych z odpadów górniczych zawierających rudy Mn, (2) niewielką mobilizację Fe i Al ekstrahowanego za pomocą szczawianu amonu w kwaśnych glebach powstałych z materiału macierzystego zawierającego skały krystaliczne (granit, gnejs) oraz (3) uwalnianie Al i Si ekstrahowanego za pomocą szczawianu amonu w glebach zawierających żużle hutnicze. Wyniki badań wskazują, że technogeniczne materiały macierzyste ulegają wietrzeniu, co najprawdopodobniej spowoduje w przyszłości zmianę składu mineralnego badanych gleb.

Zanieczyszczenie gleb pierwiastkami śladowymi określono poprzez porównanie z dopuszczalnymi zawartościami zgodnie z obowiązującymi w Polsce przepisami prawnymi. Limity te zostały przekroczone w przypadku Cu, Zn, Pb, Mo, Hg, As, Co, Ni i Ba. Grupa I badanych gleb była szczególnie wzbogacona w Co, Ni, Fe, Mn i pierwiastki ziem rzadkich. Grupa II zawierała podwyższone zawartości Cu, Zn, Hg, As, Sb, Bi, Co, Ag, Ba, Sr, U i Th, a także zawierała mniejszą zawartość pierwiastków ziem rzadkich niż grupa I. Grupa III była bogata w Cu, As, Sb, Ba, Hg, Co i Ag i zawierała najmniej pierwiastków ziem rzadkich spośród badanych gleb. Sekwencyjna ekstrakcja metodą BCR wykazała, że mobilność pierwiastków śladowych różniła się znacznie w zależności od grupy gleb, przy czym wyższą mobilność wykazywały Mn, Cu i Zn w grupie II, podczas gdy w glebach grupy I pierwiastki śladowe wstępowały głównie w formach niemobilnych. Grupa III wykazywała różnicowane formy tych pierwiastków, których mobilność kontrolowana była przez materię organiczną i tlenki Fe/Mn. Właściwości gleb (pH, zawartość węglanów i węgla organicznego) miały wpływ na mobilność pierwiastków śladowych. Wyniki przedstawione w niniejszej rozprawie przyczyniają się do poszerzenia wiedzy na temat funkcjonowania gleb technogenicznych w Tatrach oraz ich potencjalnych funkcji ekologicznych w regionach górskich. Badania dostarczają również informacji na temat stopnia zanieczyszczenia pierwiastkami śladowymi i potencjalnego ryzyka związanego z uwalnianiem się tych pierwiastków do środowiska.

Słowa kluczowe: gleby technogeniczne, pedogeneza, zanieczyszczenie gleby, środowisko górskie, historyczne górnictwo, historyczne hutnictwo

Abstract

The Tatra Mountains are a unique Central European alpine ecosystem where the non-anthropogenic soil cover and soil-forming processes are well recognized. However, the Technosols in the area's high-mountain environment have not been studied in detail to date. Therefore, this study aimed to determine the major soil-forming factors controlling soil properties and the mineralogical, micromorphological, and geochemical features of Technosols at historical mining and metallurgical sites in the Polish Tatra Mountains, in order to recognize the degree of development and contamination of these soils. Thirteen soil profiles were analysed, divided into three groups: (I) Technosols formed from mine wastes comprising Fe- and Mn-ore-bearing carbonate rocks (limestones and dolomites), (II) Technosols developed from mine wastes derived from polymetallic ore-bearing igneous and metamorphic rocks (granite, gneiss), and (III) Technosols containing wastes from smelting activity (e.g. metallurgical slags). The study involved determining soil morphology and classification, basic soil properties, magnetic susceptibility, mineral composition, micromorphological and submicromorphological features, together with pedogenic forms of Fe, Al, Si, and Mn, total contents of major elements, total contents of potentially toxic trace elements (PTTE) and their forms, and total concentrations of rare earth elements (REE).

Studied Technosols were poorly developed soils with simple soil morphology (mainly O, A, and C horizons), with a high content of rock fragments. The research has shown that the properties of Technosols in the Tatra Mountains were primarily determined by past human activities, such as mining and metallurgy, as well as the type of anthropogenic parent material, which included mine wastes and metallurgical slags, that influenced soil properties, mineral, and chemical composition. Soil formation was significantly influenced by vegetation, which was conditioned by the relief and climatic conditions dependent on altitudinal zonation. Vegetation and plant-derived soil organic matter shaped topsoil properties. The soil-forming process, acting over a few centuries in some Technosols, led to the formation of Bw horizons.

Soil thin section analysis revealed the following microscale evidences of initial soil formation: (1) formation of Fe oxide pseudomorphs due to sulphide weathering; (2) formation of pedogenic structure in the topsoil; (3) formation of pedogenic carbonate coatings in soils developed from mine wastes composed of carbonate rocks; (4) formation of pedogenic Fe and Mn oxide coatings in acidic soils developed from mine wastes composed of crystalline rocks (granite, gneiss); (5) formation of pedogenic sulphate coatings in soils containing metallurgical wastes, and (6) bioturbations (e.g. root channels and biogenic channels filled with a material reworked by soil animals). Micromorphological observations also showed that metallurgical slags in Technosols can serve as a habitat for soil fauna (most likely nematodes or enchytraeids). Selective extractions of pedogenic Fe, Al, Mn, and Si showed (1) the release of oxalate-extractable Mn in soils

developed from Mn-bearing ore mine wastes, (2) a slight mobilisation of oxalate-extractable Fe and Al in acidic Technosols developed from mine wastes composed of crystalline rocks, and (3) the release of oxalate-extractable Al and Si in Technosols containing metallurgical slags. These results indicate that technogenic parent materials undergo weathering, which will most likely consequently transform the mineral composition of the studied Technosols in the future.

Contamination of soils with PTTE was compared against Polish regulatory limits, which were exceeded for Cu, Zn, Pb, Mo, Hg, As, Co, Ni, and Ba. Group I Technosols were particularly enriched in Co, Ni, Fe, Mn, and REE. Group II soils contained elevated concentrations of Cu, Zn, Hg, As, Sb, Bi, Co, Ag, Ba, Sr, U, and Th; they also contained lower concentrations of REE compared to group I soils. Group III Technosols were rich in Cu, As, Sb, Ba, Hg, Co, and Ag and contained the lowest REE contents among the studied soils. Sequential extraction using the BCR method revealed that PTTE mobility varied strongly according to soil groups, with higher mobility of Mn, Cu, and Zn in group II soils, while group I Technosols showed mainly immobile forms of PTTE. Group III soils exhibited complex PTTE behaviour controlled by organic matter and Fe/Mn oxides. Soil properties (pH, carbonates, and TOC contents) seem to influence PTTE mobility.

This study contributes to expanding knowledge on the functioning of Technosols in the Tatra Mountains and their ecological functions in mountain regions. It also provides insights into the degree of their contamination and the potential risks associated with the release of these elements into the environment in areas of historical mining and metallurgical activities in the Tatra Mountains.

Keywords: technogenic soils, pedogenesis, soil contamination, mountain environment, historical mining, historical smelting

1. Wstęp

Badania gleb na obszarach objętych historyczną działalnością górniczą i hutniczą człowieka dostarczają cennych informacji na temat procesów glebotwórczych i długoterminowego wpływu antropogenicznych oddziaływań na środowisko. Gleby technogeniczne, wyróżniane w międzynarodowym systemie glebowym WRB jako Technosols (IUSS Working Group WRB, 2022), charakteryzują się obecnością artefaktów, które są materiałami wytworzonymi lub zmienionymi przez człowieka, a także wydobytymi w wyniku działalności górniczej (Charzyński i in., 2013; Uzarowicz i in., 2020a). Ważną kategorią wśród nich są gleby technogeniczne klasyfikowane jako Spolic Technosols, które powstają na przykład na składowiskach odpadów górniczych i przemysłowych (Néel i in., 2003; Kabała i in., 2020; Swęd i in., 2022). Gleby te powszechnie występują na współczesnych obszarach przemysłowych (Grünewald i in., 2007; Allory i in., 2022). Występują one jednak również w miejscach historycznej działalności przemysłowej, które obecnie są często pokryte roślinnością w wyniku naturalnej sukcesji roślinnej (Woś i in., 2023; Castillo Corzo i in., 2025; Uzarowicz i in., 2025). Czasami obszary te mogą obejmować środowiska wrażliwe ekologicznie i obszary chronione. Przykładem takiego miejsca są Tatry, obecnie chronione jako Tatrzański Park Narodowy (TPN).

Tatry to obszar wysokogórski położony w południowej Polsce i północnej Słowacji stanowiący część Karpat Zachodnich, który ma długą historię działalności górniczej i hutniczej (Jost, 2004; Rączkowska, 2019). Górnictwo i hutnictwo w Tatrach trwały od XV wieku do końca XIX wieku (Radwańska-Paryska i Paryski, 1995), a największy wpływ na środowisko miały w XVIII i na początku XIX wieku (Zwoliński, 1984). Działalność górnicza i hutnicza pozostawiła po sobie przekształcony krajobraz, co spowodowane było m.in. deponowaniem odpadów górniczych i żużli hutniczych na powierzchni terenu, co wpływało na lokalne środowisko. Odpady te są substratem, z którego tworzą się gleby technogeniczne (Spolic Technosols).

Dotychczasowe badania gleboznawcze w Tatrach są liczne i obejmują następujące zagadnienia związane z glebami naturalnymi (nieantropogenicznymi): (1) wpływ klimatu na właściwości gleby i tendencję do strefowości glebowej w zależności od wysokości n.p.m. (Oleksynowa i Skiba, 1977; Skiba, 1983, 1985), (2) wpływ procesów geomorfologicznych na pokrywę glebową (Drewnik, 2008), (3) cechy geochemiczne gleb (Miechówka, 1989; Oleksynowa i in., 1977), (4) skład mineralny gleb oraz przemiany

minerałów glebowych ze szczególnym uwzględnieniem minerałów ilastych (Skiba, 2007; Skiba i in., 2011; Kuligiewicz i in., 2024a, 2024b), (5) właściwości gleb organicznych i formy próchnicy glebowej (Niemyska-Łukaszuk, 1977; Miechówka i Ciarkowska, 1998; Wasak i Drewnik, 2015, 2016; Stolarczyk i in., 2024), (6) aktywność biologiczna gleby (Drewnik, 2006; Wasak, 2014; Miechówka i in., 2021), (7) zawartość pierwiastków śladowych w glebie (Miechówka i Niemyska-Łukaszuk, 2004; Wieczorek i Zadrożny, 2013; Ciarkowska i Miechówka, 2022), w których wykazano również, że historyczne wydobycie rud może wpływać na akumulację Zn, Pb i Cd w glebach nieleśnych, choć bez odniesienia do pochodzenia i funkcjonowania tatrzańskich gleb technogenicznych, (8) koncentracja radionuklidów w glebie (Kubica i in., 2002, 2007) oraz (9) klasyfikacja gleb (Komornicki i Skiba, 1996; Skiba, 1983; Strzemski, 1956). Jednak badania gleb w obszarach historycznego górnictwa i hutnictwa są bardzo rzadkie. Właściwości, skład mineralny, geneza i klasyfikacja gleb technogenicznych w Tatrach nie stanowiły dotychczas przedmiotu szczegółowych badań.

Analiza mikromorfologiczna, której celem jest rozpoznanie właściwości gleby w skali mikroskopowej, stanowi wraz z analizami chemicznymi form pedogenicznych Fe, Al, Mn i Si cenne narzędzie do badania efektów procesów glebotwórczych w glebach technogenicznych. W ciągu ostatnich dwóch dekad mikromorfologia gleby jest coraz częściej wykorzystywana do badania genezy gleb technogenicznych (Zanuzzi i in., 2009; Séré i in., 2010; Uzarowicz i Skiba, 2011; Jangorzo i in., 2013; Huot i in., 2015; Uzarowicz i in., 2017, 2018b; Watteau i in., 2017; Ortega i in., 2022). Najnowsze badania mikromorfologiczne (np. Huot i in., 2014; Watteau i in., 2018, 2025; Colombini i in., 2020; Ruiz i in., 2022; Díaz-Ortega i in., 2024) skupiały się na badaniu procesów glebotwórczych w glebach występujących w obszarach przemysłowych na terenach nizinnych i wyżynnych. Jednak podobne dane dotyczące środowisk wysokogórskich są rzadkie. Identyfikacja cech mikromorfologicznych gleby, materii organicznej gleby i cech pedogenicznych ujawnia wzajemne oddziaływanie między wpływami antropogenicznymi a naturalnymi procesami glebotwórczymi (Zaiets i Poch, 2016; Stoops i in., 2018; Verrecchia i Trombino, 2021). Wcześniejsze badania dotyczące mikromorfologii gleby w Tatrach, takie jak badania Zasońskiego i Niemyskiej-Łukaszuk (1977), Miechówki i Ciarkowskiej (1998) oraz Drewnika (2008), koncentrowały się głównie na określeniu właściwości gleb naturalnych (nieantropogenicznych). Dotychczas nie badano gleb na obszarach objętych historyczną działalnością górniczą i hutniczą.

Selektywne ekstrakcje Fe, Al, Si i Mn z gleb są często stosowane w celu rozróżnienia mineralogicznych i chemicznych form Fe, Al, Si i Mn w glebach, a także w celu określenia przemian pedogenicznych i wietrzenia minerałów, co jest pomocne w identyfikacji stopnia zaawansowania procesów glebotwórczych (McKeague i Day, 1966; Cornell i Schwertmann, 2003). Selektywne ekstrakcje Fe, Al, Si i Mn dla gleb technogenicznych powstałych z różnych antropogenicznych materiałów macierzystych (odpady popiołowo-żużlowe z elektrowni węglowych, odpady górnicze zawierające siarczki Fe i Cu; odpady górnicze z kopalń osadowych rud żelaza) wskazują na uwalnianie tych pierwiastków w środowisku glebowym i dowodzą, że wyniki ekstrakcji mogą być dobrym wskaźnikiem inicjalnych procesów glebotwórczych w glebach technogenicznych (Uzarowicz i Skiba, 2011; Uzarowicz i in., 2017, 2024, 2025). Wydaje się, że selektywne ekstrakcje Fe, Al, Si i Mn powinny być również stosowane w przypadku gleb technogenicznych powstałych z innych antropogenicznych materiałów macierzystych, w tym gleb technogenicznych w Tatrach.

Badania nad określeniem zawartości potencjalnie toksycznych pierwiastków śladowych w glebach Tatr były prowadzone przez wielu naukowców. Zbadano różnice w zawartości pierwiastków śladowych w glebach wraz ze wzrostem wysokości w rejonie Morskiego Oka i Kasprowego Wierchu (Korzeniowska i Krąż, 2020). Prowadzono również badania nad zanieczyszczeniem pierwiastkami śladowymi w polskich parkach narodowych, w tym w TPN. Analizy wykazały obecność pierwiastków śladowych w drzewostanach świerkowych (*Picea abies* (L.) H. Karst), ich akumulację w igłach, a także określiły zawartości tych pierwiastków w formach biodostępnych w glebie (Staszewski i in., 2012). Zbadano również wpływ typów siedlisk roślinnych na charakter i występowanie wybranych pierwiastków (Kwapuliński i in., 2013). Ponadto badano biodostępność pierwiastków w glebach TPN w Dolinach Chochołowskiej, Kościeliskiej, Strążyskiej i Małej Łąki (Kwapuliński i in., 2012). Badano również aktywności wybranych radionuklidów oraz zawartość pierwiastków śladowych w wierzchniej warstwie gleby w Dolinie Chochołowskiej, Kościeliskiej, Bystrej, Suchej Wody i Rybiego Potoku (Kubica i in., 2007; Stobiński i Kubica, 2017). Ponadto analizowano zawartość pierwiastków śladowych w glebach bielicowych (Kubica i in., 2007; Kowalska i in., 2021) i inicjalnych na terenie TPN (Niemyska-Łukaszuk, 1977; Miechówka i Niemyska-Łukaszuk, 2004). Zawartość pierwiastków śladowych badano również w glebach torfowisk (Miechówka i in., 2002b) oraz w glebach pastwisk górskich w TPN

(Miechówka i in., 1997). W ostatnich latach analizowano formy występowania pierwiastków w glebach na przykładzie lasów TPN (Paprotny i in., 2024). Pierwiastki śladowe badano również w wybranych glebach nieleśnych TPN (Miechówka, 2001; Miechówka i in., 2002a). Oceniono również zanieczyszczenie metalami w opadach pyłowych, pokrzywach i glebach w Dolinach Chochołowskiej i Strążyskiej oraz w pobliżu Morskiego Oka, odzwierciedlające wpływ długotrwałej emisji pierwiastków śladowych (Paukszto i Mirosławski, 2019). Analizowano także zawartości metali śladowych (Zn, Pb i Cd) w powierzchniowych warstwach gleb nieleśnych z TPN (Ciarkowska i Miechówka, 2022). Według badań przeprowadzonych na Słowacji, najpoważniejszymi zanieczyszczeniami gleby w Tatrach były Cd i Fe, a jako główne źródła zanieczyszczeń wskazano transport i turystykę (Demková i in., 2023). Pomimo rozległej wiedzy na temat zawartości pierwiastków śladowych w glebach Tatr, do tej pory nie przeprowadzono szczegółowych badań dotyczących tych pierwiastków w glebach na obszarach historycznego górnictwa i hutnictwa, w tym miejscach składowania odpadów poprzemysłowych.

2. Cel i hipotezy badawcze

Badania miały na celu analizę gleb technogenicznych na obszarach historycznego górnictwa i hutnictwa w Tatrach, aby:

1. zidentyfikować główne czynniki glebotwórcze kształtujące właściwości i rozwój gleb technogenicznych;
2. określić mikromorfologiczne, submikromorfologiczne i chemiczne wskaźniki procesów glebotwórczych;
3. ocenić stopień zanieczyszczenia i mobilność pierwiastków śladowych w badanych glebach, a także ryzyko środowiskowe związane z obecnością tych pierwiastków w glebach.

Szczegółowe cele badań są następujące.

I. Czynniki wpływające na powstawanie gleb w wysokogórskich glebach technogenicznych:
   - Określenie roli kluczowych czynników glebotwórczych (działalność człowieka, materiał macierzysty, pokrywa roślinna, ukształtowanie terenu, warunki klimatyczne, czas) w kształtowaniu właściwości wysokogórskich gleb technogenicznych;

II. Mikromorfologiczne i chemiczne wskaźniki pedogenezy:
   - Identyfikacja cech mikromorfologicznych i submikromorfologicznych w glebach technogenicznych powstałych z różnych podłoży antropogenicznych (odpady górnicze, żużle hutnicze) w Tatrach;
   - Określenie chemicznych wskaźników pedogenezy poprzez selektywną ekstrakcję Fe, Al, Mn i Si oraz określenie form tych pierwiastków w celu oceny stopnia zaawansowania procesów glebotwórczych;

III. Cechy geochemiczne i mobilność pierwiastków śladowych:
   - Określenie całkowitych zawartości pierwiastków śladowych (Cu, Zn, Pb, Cd, Mo, Hg, As, Sb, Bi, Co, Ni, Ba, Sr, Ag, Au i Sn), pierwiastków ziem rzadkich (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb i Lu) i pierwiastków promieniotwórczych (U i Th) w glebach technogenicznych na obszarach historycznego górnictwa i hutnictwa w Tatrach;
   - Ocena stopnia zanieczyszczenia gleby poprzez porównanie zawartości pierwiastków śladowych w badanych glebach z dopuszczalnymi zawartościami określonymi w polskich przepisach prawnych;

– Określenie geochemicznych form wybranych pierwiastków śladowych (Cu, Zn, Pb, Cd, As, Sb, Ba, Sr, Co, Ni, Mn i Cr) przy użyciu sekwencyjnej ekstrakcji metodą BCR oraz ocena ich mobilności w odniesieniu do właściwości gleby, takich jak pH, zawartość węglanów i zawartość glebowej materii organicznej.

Dzięki połączeniu tych podejść niniejsza praca przyczynia się do zrozumienia genezy gleb technogenicznych w środowiskach alpejskich, podkreśla ich rolę jako archiwów historycznego górnictwa oraz dostarcza nowych informacji na temat ich funkcji ekologicznych i środowiskowych w Tatrach.

Postawiono następujące hipotezy: (1) rozwój gleb technogenicznych Spolic w Tatrach jest kontrolowany przez podobne czynniki glebotwórcze, które kształtują właściwości gleb naturalnych (nieantropogenicznych), przy czym w rozwoju gleb technogenicznych najważniejszą rolę odgrywają działalność człowieka, pochodzenie i właściwości materiału macierzystego, a także roślinność, (2) gleby technogeniczne w Tatrach ulegają podobnym przemianom pedogenicznym jak gleby naturalne, a szczegółowe badania chemiczne, mineralogiczne i mikromorfologiczne pozwolą zidentyfikować pierwsze efekty procesów glebotwórczych, a także (3) gleby technogeniczne w Tatrach są w zróżnicowanym stopniu zanieczyszczone różnymi pierwiastkami śladowymi występującymi w odpadach górniczych i hutniczych, a pewna pula pierwiastków może być uwalniana do środowiska i stanowić potencjalne zagrożenie w skali lokalnej.

3. Materiały i metody

3.1. Obszar badań

Badania przeprowadzono w Tatrach, najwyższej części pasma Karpat, położonych w południowej Polsce. Tatry stanowią wyjątkowy ekosystem alpejski, obecnie chroniony jako Tatrzański Park Narodowy (TPN) i wpisany na listę światowej sieci rezerwatów biosfery UNESCO. Wysokość terenu waha się od około 900 m n.p.m. u podnóża gór do 2655 m n.p.m. na szczycie Gerlach, z wyraźnym zróżnicowaniem klimatu i roślinności w zależności od wysokości.

Klimat Tatr wyróżnia się na tle terenów otaczających i całej Polski. Średnia roczna temperatura powietrza wynosi od około 6°C u podnóża gór do -4°C w szczytowych partiach gór, a opady rosną wraz z wysokością od około 1000 mm do 1800 mm rocznie (Hess, 1996). Ten gradient klimatyczny powoduje pionowe zróżnicowanie roślinności, co wyrażone jest poprzez piętrowe ułożenie zbiorowisk roślinnych. Piętro regla dolnego jest zdominowane przez lasy mieszane z bukiem (*Fagus sylvatica*) i jodłą (*Abies alba*). W piętrze regla górnego występują lasy z dominacją świerka (*Picea abies*) i brzozy (*Betula pendula*). Wyżej występują subalpejskie zarośla kosodrzewiny (*Pinus mugo*), ponad którymi rosną alpejskie łąki, a najwyżej znajduje się piętro turni z porostami i mchami (Piękoś-Mirkowa i Mirek, 1996).

Pod względem geologicznym Tatry składają się z granitoidów w Tatrach Wysokich, skał metamorficznych (gnejsów, łupków) w Tatrach Zachodnich oraz formacji osadowych (wapieni, dolomitów, piaskowców, łupków itp.) w niższych strefach (Kotański, 1971; Gradziński i in., 2001). Rzeźba terenu jest ukształtowana przez przeszłe procesy glacjalne i obecnie działające procesy fluwialne i stokowe, tworząc złożony krajobraz dolin i grzbietów (Klimaszewski, 1996).

Mozaikowatość jest bardzo charakterystyczną cechą pokrywy glebowej w Tatrach. Właściwości gleb zależą głównie od skały macierzystej (różne skały magmowe, osadowe i metamorficzne), roślinności, procesów morfogenetycznych i warunków klimatycznych (Komornicki i Skiba, 1996). Najczęściej występującymi glebami są gleby bielicowe, rędziny, gleby brunatne, a także gleby inicjalne (litosole i regosole) (Komornicki i Skiba, 1996; Drewnik i in., 2008).

Działalność człowieka wywarła silny wpływ na środowisko górskie. Od XV do końca XIX wieku Tatry były ważnym ośrodkiem górnictwa i hutnictwa. Wydobywano i

wytapiano tam m.in. miedź, srebro, żelazo i mangan, a pozostałością po tej działalności są hałdy górnicze, składowiska żużla oraz pozostałości infrastruktury górniczej i hutniczej. Obecnie te opuszczone tereny przemysłowe porasta roślinność, a odpady górnicze i hutnicze stanowią materiały macierzyste dla gleb technogenicznych (Jost, 2004; Rączkowska, 2019).

3.2. Obiekt badań

Obiektem badań były gleby technogeniczne powstałe na terenach pogórniczych i pohutniczych w Tatrach. Gleby te charakteryzowały się obecnością artefaktów, przede wszystkim w postaci fragmentów skał wydobytych w kopalniach i zdeponowanych na powierzchni terenu, a także żużli powstałych w zakładach hutniczych. Prace terenowe przeprowadzono w ośmiu obszarach historycznego górnictwa i hutnictwa, które reprezentują najlepiej zachowane i najważniejsze typy technogenicznych materiałów macierzystych oraz etapy rozwoju działalności przemysłowej w Tatrach (Art.1: Ryc. 1 i 2, Tabela 1):

I. Huciańskie Banie (kopalnia rud manganu i żelaza) – profile 1 i 2 (P1 i P2),
II. Wylot Doliny Kościeliskiej (kopalnia rud żelaza) – P3,
III. Dolina Kościeliska w pobliżu schroniska Ornak (sztolnia poszukiwawcza rud miedzi i srebra) – P4,
IV. Dolina Pyszniańska (kopalnia rud miedzi, srebra i żelaza) – P5 i P6,
V. Żleb pod Banie na grzbiecie Ornak (kopalnia rud miedzi, żelaza i srebra) – P7 i P8,
VI. Banisty Żleb na grzbiecie Ornak (kopalnia rud miedzi, srebra, antymonu i żelaza) – P9 i P10,
VII. Dolina Kościeliska – dawny obszar hutnictwa żelaza i metali nieżelaznych w Starych Kościeliskach – P11 i P12,
VIII. Kuźnice (dawny obszar hutnictwa) – P13.

Zbadano trzynaście profili glebowych. Gleby zostały sklasyfikowane jako Spolic Technosols lub Coarsic Spolic Technosols zgodnie z międzynarodowym systemem WRB (IUSS Working Group WRB, 2022). Podzielono je na podstawie charakteru materiałów macierzystych na trzy grupy gleb:

- Grupa I: Gleby technogeniczne powstałe z odpadów górniczych stanowiących skały węglanowe (wapienie, dolomity) zawierające pozostałości rud żelaza i manganu (P1–P3),
- Grupa II: Gleby technogeniczne powstałe z odpadów górniczych stanowiących skały magmowe i metamorficzne (granit, gnejs) zawierające pozostałości rud polimetalicznych (P5–P10),
- Grupa III: Gleby technogeniczne zawierające żużle hutnicze i inne odpady pochodzące z zakładów hutniczych (P11–P13),
- Profil 4 (P4) wykazywał mieszane właściwości typowe dla gleb technogenicznych z grup I i II.

3.3. Analizy laboratoryjne

Szczegółowy opis analiz laboratoryjnych wykonanych do przygotowania niniejszej dysertacji został przedstawiony w publikacjach wchodzących w jej skład (Art. 1 – 3). W dalszej części przedstawiono skrótowy opis wykonanych analiz laboratoryjnych.

3.3.1. Podstawowe właściwości gleb

Próbki gleby pobrane z każdego poziomu glebowego zostały wysuszone w temperaturze pokojowej, a następnie przesiane na sicie 2 mm w celu oddzielenia części szkieletowych (>2 mm) i części ziemistych (<2 mm). Badania właściwości gleb przeprowadzono na częściach ziemistych zgodnie ze standardowymi procedurami gleboznawczymi (Van Reeuwijk, 2002; Pansu i Gautheyrou, 2006; Brogowski i Czerwiński, 2016; Soil Science Division Staff, 2017). Określono następujące właściwości:

- skład granulometryczny metodą Bouyoucos–Casagrande w modyfikacji Prószyńskiego (Warzyński i in., 2018); grupy granulometryczne określono zgodnie z klasyfikacją USDA;
- pH metodą potencjometryczną w H_2O i 1M KCl (stosunek masy gleby do objętości roztworu 1:2,5);
- zawartość węglanów metodą objętościową Scheiblera z użyciem 10% HCl;
- zawartość węgla organicznego (TOC), całkowitego azotu (TN) i całkowitej siarki (TS) za pomocą analizatora elementarnego CHNS;

- podatność magnetyczna za pomocą wielofunkcyjnego urządzenia MFK1-FA Kappabridge, zgodnie z procedurami Thompsona i Oldfielda (1986);
- kwasowość wymienna (EA) metodą Sokołowa;
- wymienne kationy zasadowe (EB) (Ca, Mg, K i Na) wyekstrahowano przy użyciu octanu amonu i chlorku amonu odpowiednio w próbkach glebowych niezawierających i zawierających węglany (Ostrowska i in., 1991); zawartość pierwiastków w ekstraktach określono metodą ICP-OES;
- pojemność kompleksu sorpcyjnego (CEC) obliczono jako sumę EA i EB;
- stopień wysycenia kompleksu sorpcyjnego zasadami (BS) obliczono jako udział procentowy EB w CEC.

3.3.2. Skład mineralny gleb

Skład mineralny próbek części ziemistych (<2 mm) określono metodą dyfrakcji rentgenowskiej (XRD). Wykorzystano dyfraktometr Bruker AXS D5005. Zastosowano promieniowanie CoKα o napięciu 40 kV i natężeniu prądu 30 mA. Zmielone próbki proszkowe były badane w zakresie od 3 do 70 º2θ przy czasie zliczania wynoszącym 1 s na każdy krok 0,02º na obrotowym stoliku. Analizy XRD przeprowadzono w Katedrze Gleboznawstwa, Instytutu Rolnictwa, Szkoły Głównej Gospodarstwa Wiejskiego (SGGW) w Warszawie.

3.3.3. Analizy mikromorfologiczne

Próbki o nienaruszonej strukturze pobrano do puszek Kubiëny z wybranych poziomów glebowych. Próbki wysuszono na powietrzu, a następnie impregnowano żywicą epoksydową Araldite 2020. Z impregnowanych bloków glebowych przygotowano polerowane płytki cienkie (szlify) o grubości 30 µm. Płytki cienkie badano w świetle przechodzącym pod mikroskopami petrograficznymi. Zastosowano opis mikromorfologiczny i terminologię według Stoopsa (2021). Płytki cienkie wykonano na Wydziale Geologii Uniwersytetu Warszawskiego.

3.3.4. Analizy SEM-EDS

Wybrane płytki cienkie z gleb analizowano za pomocą skaningowego mikroskopu elektronowego wyposażonego w spektrometr rentgenowski z analizatorem dyspersji energii (SEM-EDS). Przed analizą SEM-EDS próbki napylono węglem. Wykorzystano mikroskop skaningowy SIGMA (Zeiss) z emisją polową. Mikroskop był wyposażony w

detektor elektronów wstecznie rozproszonych (BSE). Badania przeprowadzono w trybie wysokiej próżni przy napięciu przyspieszającym 20 kV. Analizy przeprowadzono w Laboratorium Mikroskopii Elektronowej, Mikroanalizy i Dyfrakcji Rentgenowskiej Wydziału Geologii Uniwersytetu Warszawskiego.

3.3.5. Pedogeniczne formy Fe, Al, Si i Mn

Na próbkach części ziemistych przeprowadzono selektywne ekstrakcje Fe, Al, Mn i Si w celu scharakteryzowania pedogenicznych form tych pierwiastków. Wykonano następujące analizy:

- Ekstrakcja ditionianowo-cytrynianowo-wodorowęglanowa (DCB) w celu oznaczenia wolnych tlenków żelaza (Fe_d) (Mehra i Jackson, 1958);
- Ekstrakcja roztworem 0,175 M szczawianu amonu i 0,1 M kwasu szczawiowego, o pH 3,0 w ciemności w celu oznaczenia amorficznych i słabo wykrystalizowanych form Fe, Al, Mn i Si (Fe_{ox}, Al_{ox}, Mn_{ox}, Si_{ox}) (Schwertmann, 1964).

Zawartości badanych pierwiastków zmierzono metodą ICP–OES. Całkowitą zawartość Fe (Fe_t) określono poprzez całkowitą mineralizację mikrofalową części ziemistych za pomocą stężonych kwasów (HNO_3, HF, HCl, $HClO_4$), a następnie analizę ekstraktów metodą ICP-OES. Wszystkie analizy przeprowadzono w dwóch powtórzeniach.

Na podstawie tych danych obliczono następujące parametry: $Fe_{nf} = Fe_t - Fe_d$, $Fe_c = Fe_d - Fe_{ox}$, Fe_d/Fe_t, Fe_{ox}/Fe_d, $Al_{ox} + ½Fe_{ox}$ (ten ostatni wyrażony w %).

3.3.6. Całkowita zawartość pierwiastków głównych, śladowych i pierwiastków ziem rzadkich

Oznaczono całkowitą zawartość pierwiastków głównych (Si, Fe, Al, Mg, Ca, K i Mn), pierwiastków śladowych (Cu, Zn, Pb, Cd, Mo, Hg, As, Sb, Bi, Co, Ni, Ba, Sr, Ag, Au, Sn), pierwiastków promieniotwórczych (U, Th) oraz pierwiastków ziem rzadkich (Sc, Y oraz lantanowce od La do Lu). Próbki zostały zmielone i stopione z dodatkiem $LiBO_2$ i $Li_2B_4O_7$, a następnie stopy rozpuszczono w HNO_3. Zawartość pierwiastków głównych i śladowych została zbadana odpowiednio metodą ICP–AES i ICP–MS. Analizy wykonano w Bureau Veritas Minerals Laboratories (BVML) w Kanadzie.

3.3.7. Sekwencyjna ekstrakcja pierwiastków śladowych metodą BCR

Operacyjnie zdefiniowane formy chemiczne wybranych pierwiastków śladowych (Cu, Zn, Pb, Cd, As, Sb, Ba, Sr, Co, Ni, Mn i Cr) zostały określone w próbkach glebowych przy użyciu czterostopniowej sekwencyjnej procedury ekstrakcji metodą BCR (Rauret i in., 1999; Mossop i Davidson, 2003) (Art. 3: Tabela 1). Zawartość pierwiastków w ekstraktach glebowych uzyskanych podczas kolejnych etapów ekstrakcji określono metodą ICP–OES. Ekstrakty glebowe analizowano w dwóch powtórzeniach. Próbki kontrolne analizowano w dwóch powtórzeniach z każdym zestawem frakcji. Analizy przeprowadzono w Katedrze Gleboznawstwa i Chemii Rolniczej, Wydziału Nauk Ścisłych Uniwersytetu w Granadzie w Hiszpanii.

3.3.8. Analizy statystyczne

W celu zidentyfikowania czynników determinujących właściwości badanych gleb oraz rozróżnienia grup gleb o podobnych właściwościach zastosowano analizę składowych głównych (PCA). Przed analizą statystyczną dane zostały znormalizowane, a w analizie uwzględniono następujące właściwości: podatność magnetyczna (χ), pH_{H2O}, zawartość węglanów ($CaCO_3$ eq.), EA, EB, BS, a także zawartość wybranych pierwiastków głównych przeliczonych na tlenki (SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, K_2O i MnO).

Zależność między zawartościami pierwiastków śladowych we frakcjach zdefiniowanych operacyjnie (analiza sekwencyjna metodą BCR) a wybranymi właściwościami gleb (pH, zawartość węglanów i TOC) oceniono za pomocą korelacji rang Spearmana. Występowanie rozkładu normalnego w danych sprawdzono za pomocą testu Shapiro-Wilka. Poziom istotności (α) w niniejszym badaniu wynosił 0,05. Analizy statystyczne przeprowadzono w programie Statistica^{TM} 13.3 (Tibco Software Inc.).

4. Wyniki

4.1. Morfologia i podstawowe właściwości gleb technogenicznych

Badane gleby zostały sklasyfikowane jako Spolic Technosols i Coarsic Spolic Technosols (Art. 1: Tabela 1). Charakteryzowały się one prostą morfologią profili glebowych (najczęściej o układzie poziomów O–A–C, z wyjątkiem P5 i P6, które posiadały poziomy Bw) i wysokim udziałem części szkieletowych (większość poziomów glebowych zawierała ponad 50% fragmentów skalnych, jednak liczne poziomy zawierały nawet do 90% fragmentów skalnych). Części ziemiste gleb (< 2 mm) miały uziarnienie piasku gliniastego i gliny piaszczystej (Art. 1: Tabela 2).

W grupie I gleb technogenicznych pH wynosiło od 7,2 do 8,1 (poziomy mineralne). Zawartość węglanów była wysoka (do 31% $CaCO_3$). Średnie wartości TOC w poziomach organicznych wynosiły 42,5%, a TN 1,36%, przy niższych wartościach w warstwach mineralnych (średnio TOC 4,35% i TN 0,27%). Średnia zawartość TS i TP w całych profilach wynosiła odpowiednio 0,06% i 0,30%. Wartości podatności magnetycznej wahały się od 7 do 91 $\times 10^{-8} \cdot m^3 \cdot kg^{-1}$ (Art. 1: Tabela 2). EA i EB w całych profilach wynosiły średnio odpowiednio 0,33 i 41,28 $cmol(+) \cdot kg^{-1}$, natomiast BS wynosiło powyżej 97,2% we wszystkich poziomach glebowych (Art. 1: Tabela 3).

W grupie II gleb technogenicznych pH wynosiło między 3,8 a 6,0 (poziomy mineralne). Nie stwierdzono obecności węglanów. W poziomach organicznych średnia zawartość TOC wynosiła 39,3%, a TN 1,39%; w poziomach mineralnych średnia zawartość TOC wynosiła 2,17%, a TN 0,15%. Średnia zawartość TS i TP w całych profilach wynosiła odpowiednio 0,16% i 0,10%. Wartości podatności magnetycznej wynosiły od 10 do 39 $\times 10^{-8} \cdot m^3 \cdot kg^{-1}$ (Art. 1: Tabela 2). EA i EB w całych profilach wynosiły średnio odpowiednio 6,24 i 6,16 $cmol(+) \cdot kg^{-1}$, natomiast BS wynosiło od 4,7 do 99,9 % (Art. 1: Tabela 3).

W glebach technogenicznych grupy III pH wynosiło od 5,6 do 8,6 (poziomy mineralne). Średnia zawartość węglanów wynosiła 3%. Średnia zawartość TOC w poziomach organicznych wynosiła 42,64%, a TN 1,20%, natomiast w poziomach mineralnych średnia zawartość TOC wynosiła 6,73% (do 14,7% w poziomie 2C w P12 wzbogaconej w węgiel drzewny), a TN 0,29%. Podatność magnetyczna była wyjątkowo wysoka, osiągając nawet 10486 $\times 10^{-8} \cdot m^3 \cdot kg^{-1}$ (Art. 1: Tabela 2). EA i EB w całych

profilach wynosiły średnio odpowiednio 0,09 i 24,87 cmol(+)·kg^{-1}, natomiast BS było w profilach P11–P13 wyższe niż 94,6% (Art. 1: Tabela 3).

W profilu 4 średnia wartość pH wynosiła 6,6, przy braku węglanów. Średnia wartość TOC wynosiła 3,06%, TN 0,22%, TS 0,03% i TP 0,06% w całym profilu. Wartości podatności magnetycznej wynosiły od 8 do 22 ×10^{-8}·m^{3}·kg^{-1} (Art. 1: Tabela 2). EA i EB w całym profilu wynosiły średnio odpowiednio 0,06 i 14,67 cmol(+)·kg^{-1}, natomiast BS było wyższe niż 99,40% (Art. 1: Tabela 3).

4.2. Skład mineralny gleb na podstawie analizy XRD

Skład mineralny badanych gleb technogenicznych odzwierciedlał różnorodność ich materiałów macierzystych (Art. 1: Tabela 4). W glebach technogenicznych z grupy I dominowały kalcyt i kwarc, a także skalenie (albite, ortoklaz), mika i hematyt. Zidentyfikowano również dolomit i minerały ilaste (prawdopodobnie smektyt lub wermikulit). Gleby technogeniczne z grupy II i profil 4 charakteryzowały się obecnością kwarcu, miki, skaleni (ortoklazu i albitu) oraz jarosytu. Stwierdzono również obecność domieszek chlorytu, pirytu i amfiboli. W składzie mineralnym gleb technogenicznych z grupy III dominował kwarc, któremu towarzyszyły magnetyt, hematyt, skalenie fayalitowe (albit i ortoklaz), mika i minerały ilaste (smektyt, wermikulit, kaolinit, chloryt), natomiast występowały również domieszki wüstytu, goethytu, dolomitu i kalcytu.

4.3. Cechy mikromorfologiczne i submikromorfologiczne

Gleby technogeniczne z grupy I (P1–P3) składały się z fragmentów skał osadowych węglanowych (wapienie, dolomity) z domieszką skał osadowych krzemionkowych i drobnego materiału glebowego występującego pomiędzy fragmentami skał (Art. 2: Ryc. 1A–F, Tabela 2). Materiał glebowy charakteryzował się wewnątrz agregatową mikrostrukturą (intergrain microaggregate microstructure). Masa podstawowa (groundmass) występowała w postaci agregatów okruchowych (crumbs) lub foremno-wielościennych zaokrąglonych (subangular blocky aggregates) o wskaźniku rozmieszczenia c/f porfirik (porphyric) (Art. 2: Ryc. 1A i B; Tabela 2). Fragmenty skał węglanowych, żelazistych i krzemionkowych, a także ziarna węglanów, kwarcu i skaleni stanowiły gruboziarniste fragmenty w agregatach. Zidentyfikowano pseudomorfozy tlenku żelaza po siarczkach (wybrane przedstawiono w Art. 2: Ryc. 1E i F, Ryc. 2A).

Mikromasa gleb była materiałem złożonym z minerałów ilastych i tlenków żelaza o różnorodnej strukturze-b (undifferentiated b-fabric). W cienkich płytkach z gleb sporadycznie znajdowano korzenie. Sporadycznie stwierdzono również otoczki wtórnych węglanów wapnia (Art. 2: Ryc. 1G i H).

Gleby technogeniczne z grupy II (P5–P10) powstały z odpadów górniczych zawierających fragmenty skał magmowych (granit) i metamorficznych (gnejs). W glebach dominowała złożona mikrostruktura współwystępująca z ziarnistymi agregatami (granular aggregates) (Art. 2: Ryc. 3 A–J, Tabela 2). Masa glebowa miała wskaźnik rozmieszczenia c/f monic (monic) (Art. 2: Tabela 2). Składała się z mikroagregatów glebowych, ziaren minerałów oraz słabo zwietrzałych fragmentów skał składających się z glinokrzemianów (skalenie, miki, chloryt), kwarcu, barytu i tlenków żelaza (Art. 2: Ryc. 3G i H, Ryc. 7). Dominującymi ziarnami mineralnymi były kwarc, muskowit, biotyt, drobnoziarnista mika (sericit), chloryt i tlenki żelaza (Art. 2: Ryc. 3I i J, Tabela 2). Siarczki żelaza występowały rzadko (Art. 2: Ryc. 2B). Mikromasa składała się z minerałów ilastych i tlenków żelaza i miała różnorodną (undifferentiated) i okołoziarnistą (granostriated b-fabric) strukturę-b (Art. 2: Ryc. 3C i D). Dominowały dobrze rozwinięte okruchowe agregaty (Art. 2: Ryc. 3E i F). Sporadycznie obserwowano otoczki zawierające tlenki żelaza na fragmentach skał (np. Art. 2: Ryc. 3A i B). Mapa pierwiastkowa w SEM-EDS dla Mn (Art. 2: Ryc. 7) ujawniła występowanie otoczek złożonych z faz zawierających Mn (najprawdopodobniej tlenków Mn), które wydają się mieć pochodzenie pedogeniczne. Ponadto stwierdzono również bioturbacje w postaci kanałów wypełnionych materiałem glebowym, który najprawdopodobniej został przerobiony przez faunę glebową (np. Art. 2: Ryc. 3G i H).

Gleby technogeniczne z grupy III (P11–P13) zawierały odpady z zakładów hutniczych, w tym żużle, jako główny substrat glebowy. Mikrostruktura tych gleb była złożona z ziarnistych mikroagregatów (granular microaggregates) (Art. 2: Ryc. 4 A–J, Tabela 2). Masa glebowa składała się głównie z fragmentów żużli hutniczych z zagłębieniami często zamieszkanymi przez organizmy glebowe (najprawdopodobniej nicienie lub wazonkowce) i wypełnionymi mikromasą glebową przerobioną przez te zwierzęta (Art. 2: Ryc. 4A i B). Żużle składały się m in. z piroksenu i magnetytu (Art. 2: Ryc. 4G i H), ale niektóre z nich były materiałami amorficznymi (Art. 2: Ryc. 4I i J, Tabela 2) lub zawierały igiełkowate fazy zawierające Fe (najprawdopodobniej tlenki Fe) (Art. 2: Ryc. 8). Masa glebowa składała się prawdopodobnie z minerałów ilastych, ale

zawierała również znaczny udział siarki i fosforu, co sugeruje obecność związków organicznych. Typowymi gruboziarnistymi składnikami masy glebowej były sferyczne tlenki żelaza, najprawdopodobniej magnetyt (Art. 2: Ryc. 2C). Ciemny kolor gleby był związany z obfitością fragmentów węgla drzewnego (Art. 2: Ryc. 2C) oraz materią organiczną pochodzenia antropogenicznego rozproszoną w mikromasie. Mapa pierwiastkowa w SEM-EDS dla siarki (Art. 2: Ryc. 8) ujawniła obecność otoczek zawierających S, najprawdopodobniej w formie siarczanów. W glebach sporadycznie znajdowano resztki roślinne w różnych stanie rozkładu. Znaleziono także agregaty materiału glebowego zawierającego minerały ilaste, które najprawdopodobniej powstały w wyniku zmieszania gleby rodzimej z materiałem antropogenicznym powstałym podczas działalności hutniczej (Art. 2: Ryc. 4A–F).

Materiał macierzysty profilu 4 stanowiła mieszanka węglanowych skał osadowych, skał magmowych i metamorficznych. Podłoże glebowe charakteryzowało się foremno-wielościenną zaokrągloną mikrostrukturą (subangular blocky microstructure) (Art. 2: Ryc. 5A–D, Tabela 2). Masa glebowa miała wskaźnik rozmieszczenia c/f porfirik (porphyric) i różnorodną strukturę-b (undifferentiated b-fabric) (Art. 2: Ryc. 5A–D). Składała się z glinokrzemianowego materiału gliniastego z domieszką tlenków żelaza (Art. 2: Ryc. 2D). Materiał gruboziarnisty reprezentowały fragmenty kwarcu, skaleni, węglanów, miki (Art. 2: Ryc. 5A i B, Tabela 2) oraz tlenków żelaza (Art. 2: Ryc. 2D). Materia organiczna składała się z ciemnobrązowych pozostałości organicznych rozproszonych w mikromasie i kanałach. Kanały były często wypełnione korzeniami (Art. 2: Ryc. 5C i D).

4.4. Pedogeniczne formy Fe, Al, Mn i Si

Zawartość Fe_t wahała się od 7484 do 344307 $mg \cdot kg^{-1}$, Fe_d od 1273 do 50639 $mg \cdot kg^{-1}$, a Fe_{ox} od 499 do 93449 $mg \cdot kg^{-1}$ we wszystkich profilach (Art. 2: Tabela 3). Wśród grup gleb zaobserwowano wyraźne różnice w stosunkach Fe_d/Fe_t i Fe_{ox}/Fe_d. W grupie I stosunki Fe_d/Fe_t i Fe_{ox}/Fe_d wynosiły średnio odpowiednio 0,38 i 0,22, podczas gdy w grupie II średnia tych stosunków wynosiła 0,32. W profilu 4, charakteryzującym się cechami grup I i II, stosunek Fe_d/Fe_t i Fe_{ox}/Fe_d wynosił średnio odpowiednio 0,41 i 0,18, podczas gdy w grupie III stosunki te wynosiły średnio odpowiednio 0,23 i 1,26.

Zawartość Al_{ox}, Si_{ox} i Mn_{ox} różniła się między grupami gleb. W glebach technogenicznych grupy I zawartość Al_{ox} wynosiła średnio 1578 $mg \cdot kg^{-1}$, Si_{ox} 225 $mg \cdot kg^{-}$

^{1}, a Mn_{ox} 17699 mg·kg^{-1}, podczas gdy w glebach grupy II zawartość tych pierwiastków wynosiła średnio odpowiednio 1747, 156 i 2136 mg·kg^{-1}. W profilu 4 zawartość Al_{ox}, Si_{ox} i Mn_{ox} wynosiła średnio 1018, 147 i 563 mg·kg^{-1}, natomiast w grupie III Technosols ich zawartość wynosiła średnio odpowiednio 3298, 3565 i 3758 mg·kg^{-1}.

Wartości Al_{ox} + ½Fe_{ox} były niskie w grupach I i II oraz w profilu 4 (średnio 0,29%), ale znacznie wyższe w grupie III (średnio 2,70%).

4.5. Całkowite zawartości pierwiastków głównych

W ogólnym ujęciu krzem był dominującym pierwiastkiem w badanych glebach (do 66,3% SiO_2) (Art. 1: Ryc. 4). W profilach glebowych 4–13 ważnym pierwiastkiem był również Al. W składzie chemicznym profili 4–10 występowały również ogólnie wyższe zawartości K niż w innych glebach. Gleby z grupy III charakteryzowały się bardzo dużą zmiennością składu chemicznego w obrębie profilu. Oprócz Si i Al, w składzie chemicznym profili 11 i 12 występował wysoki udział Fe. Najwyższe zawartości Mg i Ca odnotowano w glebach technogenicznych grupy I. Wysokie zawartości Ca wykryto również w profilu 13, gdzie pod warstwą żużlu znajdowała się warstwa podglebia zawierająca węglany. Znaczący udział Mn odnotowano w profilach 1 i 2 (gleby technogeniczne grupy I).

4.6. Całkowite zawartości pierwiastków śladowych i pierwiastków ziem rzadkich

Zawartości pierwiastków śladowych i pierwiastków ziem rzadkich (Art. 3: Ryc. 1 i 2) były zróżnicowane w poszczególnych grupach gleb.

W grupie I najbardziej charakterystyczną cechą była podwyższona zawartość Co (do 205 mg·kg^{-1}) i Ni (do 431 mg·kg^{-1}), znacznie przekraczające zawartości występujące w grupach II i III. Gleby te zawierały stosunkowo niskie ilości innych pierwiastków śladowych, chociaż Zn, Mo i Sr wykazywały podwyższone zawartości w porównaniu z glebami w innych badanych lokalizacjach. Grupa I zawierała generalnie najwyższe zawartości pierwiastków ziem rzadkich w porównaniu z innymi glebami (od 61 do 786 mg·kg^{-1}) (Art. 3: Tabela 2).

Grupa II wykazywała bardzo duże zróżnicowanie zawartości pierwiastków śladowych, ze szczególnie wysokimi ilościami następujących pierwiastków: do 20 mg·kg^{-1} Mo, 32277 mg·kg^{-1} Ba, 581 mg·kg^{-1} Sr, 15 mg·kg^{-1} U, 23 µg·kg^{-1} Au, 1666

$mg \cdot kg^{-1}$ Cu, 159 $mg \cdot kg^{-1}$ Zn, 37 $mg \cdot kg^{-1}$ Hg, 347 $mg \cdot kg^{-1}$ As, 1263 $mg \cdot kg^{-1}$ Sb, 21 $mg \cdot kg^{-1}$ Bi, 70 $mg \cdot kg^{-1}$ Co, 25 $mg \cdot kg^{-1}$ Th oraz >100 $mg \cdot kg^{-1}$ Ag. Całkowita zawartość pierwiastków ziem rzadkich wynosiła od 61 do 346 $mg \cdot kg^{-1}$ (Art. 3: Tabela 2).

Największe zróżnicowanie składu pierwiastkowego wystąpiło w glebach technogenicznych z grupy III. Zawartość wszystkich badanych pierwiastków w profilach 11 i 13 była zazwyczaj niska w porównaniu z innymi glebami. Profil 12 wykazywał wysoką całkowitą zawartość As, Cu, Sb i Ba w całym profilu glebowym, jednak poziom 3C w tym profilu zawierał ekstremalne ilości Cu (>10000 $mg \cdot kg^{-1}$), Hg (>50 $mg \cdot kg^{-1}$), As (901 $mg \cdot kg^{-1}$), Sb (>2000 $mg \cdot kg^{-1}$), Bi (44 $mg \cdot kg^{-1}$), Ag (>100 $mg \cdot kg^{-1}$) i Au (2172 $\mu g \cdot kg^{-1}$). Gleby charakteryzowały się najniższą całkowitą zawartością pierwiastków ziem rzadkich wynosząc od 59 do 237 $mg \cdot kg^{-1}$ (Art. 3: Tabela 2).

Profil 4 wykazywał umiarkowane zawartości pierwiastków śladowych (np. Zn, Cr, Pb, As, Co, Ni, Ba, przy stosunkowo niskiej ilości np. Cu, Cd, Mo, Hg, Sb, Bi, Ag i Au. Całkowita zawartość pierwiastków ziem rzadkich wynosiła od 159 do 214 $mg \cdot kg^{-1}$ (Art. 3: Tabela 2).

4.7. Geochemiczne formy wybranych pierwiastków śladowych

Sekwencyjna ekstrakcja metodą BCR ujawniła duże zróżnicowanie form pierwiastków śladowych w badanych grupach gleb technogenicznych (Art. 3: Ryc. 3–5).

Grupa I charakteryzowała się dominacją Cu, Zn, Pb, As, Co, Ni i Cr we frakcji 4 (F4), co wskazuje na niską mobilność. Antymon wykazywał dużą różnorodność form i występował głównie w F4, F3 i F2, z zauważalnym udziałem w F1. Kadm, Ba, Sr i Mn często występowały w F2, z zauważalnym udziałem w F1.

Grupa II wykazywała bardziej mobilne formy. Miedź, Pb, Ba, Sr, Co, Ni, Mn i Cr występowały głównie w F2, z zauważalnym udziałem niektórych z nich w F1, podczas gdy Zn, Cd, As i Sb były częściowo ustabilizowane w F4. Kilka wyjątków odzwierciedlało zmienność charakterystyczną dla poszczególnych poziomów, np. wyższy udział Cu i Ni w F3 lub Zn, As i Sb w F2 w niektórych poziomach.

Grupa III wykazywała najbardziej zróżnicowane formy występowania pierwiastków śladowych. Miedź była rozłożona między F3 i F2, Zn i Pb występowały głównie w F2, ale także w F4, natomiast Cd dominowało w F2 i F4. Arsen i Sb występowały głównie w F4, ale pojawiały się również w F2 w wybranych poziomach.

Bar, Sr, Co, Ni i Mn występowały najobficiej w F2, natomiast Cr występował najczęściej w F2 i F4.

Profil 4 wykazywał zróżnicowane cechy, z Cu, Zn, Pb, Ba, Sr, Co, Ni i Mn dominującymi w F2, ale Cd, As, Sb i Cr częściowo ustabilizowanymi w F4.

5. Dyskusja

5.1. Czynniki glebotwórcze kontrolujące właściwości wysokogórskich gleb technogenicznych

Kluczowym czynnikiem glebotwórczym odpowiedzialnym za powstanie badanych gleb technogenicznych była działalność człowieka w przeszłości. Bez wydobycia i hutnictwa, a także przede wszystkim składowania odpadów przemysłowych, górniczych i hutniczych na powierzchni ziemi, badane gleby technogeniczne nie istniałyby. Działalność człowieka wpływa na rodzaj, ilość i rozmieszczenie materiałów antropogenicznych tworzących podłoże glebowe.

Wiele wcześniejszych badań wykazało, że skała macierzysta jest najważniejszym czynnikiem glebotwórczym kontrolującym zmienność i właściwości gleb w Tatrach (Komornicki i Skiba, 1996; Miechówka i in., 1997; Skiba i in., 2004; Wasak-Sęk, 2017). Wyniki przedstawione w pracy wskazują, że dotyczy to również gleb technogenicznych występujących w tym regionie. Rodzaj materiału macierzystego determinował cechy badanych gleb technogenicznych, takie jak właściwości fizyczne gleby (zawartość części szkieletowych, skład granulometryczny), właściwości chemiczne (zawartość węglanów w glebie, pH gleby) i właściwości sorpcyjne (np. CEC i BS), podatność magnetyczna, a także skład mineralny i chemiczny.

W wyniku rozwoju pokrywy roślinnej na obszarach pogórniczych i pohutniczych w Tatrach w przypowierzchniowych częściach gleby zakumulowała się glebowa materia organiczna (Art. 1 Ryc. 2) co wpłynęło na strukturę gleby (Art. 1: Ryc. 3) oraz pH gleby. Na przykład akumulacja igieł świerka (np. w Żlebie pod Banie) i kosodrzewiny (np. w Banistym Żlebie) spowodowała zakwaszenie górnych części gleby niezależnie od materiału macierzystego (Art. 1: Tabela 2). Ponadto glebowa materia organiczna zgromadzona w wierzchniej warstwie gleby wpłynęła na właściwości sorpcyjne gleby (Art. 1: Tabela 3). Ponadto akumulacja glebowej materii organicznej może również mieć wpływ na aktywność i różnorodność mikroorganizmów glebowych, co powinno być przedmiotem dalszych badań.

W środowiskach alpejskich, w tym w Tatrach, wysokość nad poziomem morza wpływa na warunki klimatyczne i określa strefowość klimatyczno-roślinną (Skiba, 1977). Klimat wpływa na szatę roślinną, które z kolei wpływa na właściwości gleby. Wpływ klimatu i roślinności na badane gleby można zaobserwować na zboczach Ornaku. Profile

7 i 8 (Żleb Pod Banie) oraz profile 9 i 10 (Banisty Żleb) znajdowały się w różnych strefach klimatyczno-roślinnych. Pierwsze gleby były pokryte lasem świerkowym i w dużej mierze mchami (*Bryophyta sp.*), podczas gdy drugie były zdominowane przez zarośla kosodrzewiny. Gleby profili 7–10 zawierały podobną zawartość TOC w poziomach O. Jednak w profilach 7 i 8 poziomy A były zauważalnie bogatsze w TOC niż poziomy A z profili 9 i 10. Ponadto stosunek C/N był niższy w profilach 7 i 8 niż w 9 i 10 (Art. 1: Tabela 2). Cechy takie są związane z różnicami w tempie rozkładu materii organicznej gleby, które jest wolniejsze powyżej górnej strefy leśnej w glebach tatrzańskich (Drewnik, 2002, 2006).

Innym ważnym czynnikiem wpływającym na kształtowanie się gleb w Tatrach są warunki geomorfologiczne (rzeźba terenu), które oddziałują na gleby np. poprzez nachylenie zboczy i ekspozycję (Drewnik, 2008). Pokrywa roślinna, nawet na bardziej stromych zboczach, skutecznie chroniła powierzchnię ziemi przed erozją. Ekspozycja zbocza i ilość promieniowania słonecznego wpływają na warunki mikroklimatyczne, które z kolei wpływają na zasięg górskich stref klimatyczno-roślinnych (Komornicki i Skiba, 1996). Na podstawie uzyskanych wyników wpływ warunków klimatycznych i rzeźby terenu na badane gleby jest pośredni. Klimat i ukształtowanie terenu determinują szatę roślinną, które z kolei kształtuje właściwości gleby.

Czas powstawania gleby jest również czynnikiem wpływającym na jej właściwości i stopień ukształtowania. W przypadku badanych gleb wpływ czasu jest trudny do określenia, ponieważ inne czynniki, takie jak podłoże skalne, ukształtowanie terenu, roślinność zależna od klimatu, poprzez swój decydujący wpływ na kształtowanie się właściwości gleby, utrudniają ocenę wpływu czasu. Jednakże profile 5 i 6 z poziomami Bw znajdowały się w Dolinie Pyszniańskiej, gdzie wydobycie prowadzono w XV wieku (w pozostałych miejscach wydobycie odbywało się głównie w XVIII i XIX wieku). Można zatem sądzić, że profile 5 i 6 to najstarsze ze wszystkich badanych gleb. Dlatego też powstawanie poziomów Bw może być związane z długim okresem pedogenezy.

5.2. Mikromorfologiczne, submikromorfologiczne i chemiczne wskaźniki pedogenezy gleb technogenicznych

5.2.1. Mikromorfologiczne i submikromorfologiczne wskaźniki pedogenezy

Badane gleby technogeniczne reprezentują gleby początkowego etapu procesów glebotwórczych, co potwierdza słaby stopień ukształtowania profili glebowych. Niemniej

jednak dzięki badaniom mikroskopowym określono efekty transformacji i reorganizacji technogenicznego substratu glebowego, które można traktować jako mikromorfologiczne wskaźniki pedogenezy. Pomimo młodego wieku gleb (200–500 lat) i słabego rozwoju profilu, procesy wietrzenia, a także procesy glebotwórcze i biologiczne przekształcają podłoże technogeniczne w funkcjonującą glebę. Zidentyfikowane wskaźniki obejmują tworzenie się (1) pseudomorfoz tlenku żelaza w wyniku wietrzenia siarczków; (2) struktury pedogenicznej w przypowierzchniowych poziomach gleb; (3) otoczek węglanowych w odpadach górniczych bogatych w węglany; (4) otoczek tlenku żelaza i manganu w kwaśnych glebach z odpadów górniczych zawierających skały magmowe i metamorficzne; (5) otoczek siarczanowych w glebach zawierających żużle hutnicze; oraz (6) bioturbacji wskutek działalności roślin i zwierząt.

Pseudomorfozy tlenku żelaza po siarczkach (znalezione w P1–P10) wskazują na aktywne wietrzenie chemiczne, które jest najważniejszym procesem w transformacji siarczków żelaza (Néel i in., 2003; Uzarowicz i Skiba, 2011; Uzarowicz i in., 2024). Pseudomorfozy powstają w wyniku utleniania siarczków, czego efektem jest uwolnienie do gleb żelaza oraz jonów siarczanowych. Większość pseudomorfoz w badanych glebach stanowiły całkowite pseudomorfozy składające się wyłącznie z tlenku żelaza, co sugeruje dobre napowietrzenie gleby dzięki dużej ilości szkieletu glebowego, co umożliwia wymianę powietrza (Hayes i in., 2014).

Analiza mikromorfologiczna wykazała, że w górnych częściach badanych profili glebowych tworzy się pedogeniczna struktura, co jest efektem łączenia się cząstek materiału glebowego w agregaty glebowe. Gleby technogeniczne w pierwszym etapie powstawania są zazwyczaj utworami o masywnej strukturze (Uzarowicz i in., 2018a, 2025; Watteau i in., 2019), jednakże organizmy glebowe i glebowa materia organiczna sprzyjają tworzeniu się struktury już w ciągu pierwszych kilku lat pedogenezy (Badin i in., 2009; Séré i in., 2010). Glebowa materia organiczna ma kluczowe znaczenie dla stabilności agregatów (Jangorzo i in., 2013, 2014; Watteau i in., 2019), a rozwój struktury po 15–40 latach jest porównywalny z glebami naturalnymi (Ortega i in., 2022). Aktywność biologiczna sprzyja tworzeniu agregatów (Hedde i in., 2019), a duże znaczenie ma również obecność węglanu wapnia (Uzarowicz i in., 2018b).

W odpadach górniczych zawierających skały węglanowe zidentyfikowano otoczki złożone z pedogenicznych węglanów. W badanych glebach powstają one w wyniku wytrącania się $CaCO_3$ z roztworów glebowych, często po wstępnym rozpuszczeniu

węglanów pochodzących z materiału macierzystego (Zamanian i in., 2016; Kowalska i in., 2020). Pedogeniczne węglany zidentyfikowano w glebach technogenicznych pochodzących z popiołów i osadów przemysłowych (Huot i in., 2014; Uzarowicz i in., 2017; Uzarowicz i in., 2018a; Konstantinov i in., 2020; Uzarowicz i in., 2024). Ich obecność potwierdza wietrzenie materiałów technogenicznych bogatych w wapń.

W kwaśnych glebach technogenicznych zaobserwowano występowanie otoczek tlenku żelaza na powierzchniach minerałów i skał (P5 i P6, poziomy Bw i ABw). Wskazują one na uwalnianie żelaza do gleby w wyniku przemian minerałów glebowych (Van Ranst i in., 2018; Cornell i Schwertmann, 2003), co prawdopodobnie jest związane z pewnym zaawansowanym procesem glebotwórczym (bielicowanie lub brunatnienie). Obecność otoczek tlenku żelaza w poziomach Bw sugeruje, że kilka stuleci trwania procesu glebotwórczego (gleby z poziomami Bw znajdowały się w Dolinie Pyszniańskiej, gdzie prawdopodobnie w XV wieku prowadzono działalność górniczą) wystarczyło, aby rozpocząć zaawansowane procesy glebotwórcze. W badanych glebach zidentyfikowano również rzadziej występujące otoczki tlenku manganu. Ich powstawanie zależy najprawdopodobniej od pH, warunków redoks i aktywności mikrobiologicznej (McKenzie, 1989; Eswaran i Raghu Mohan, 1973; Sullivan i Koppi, 1992; Eren i in., 2014; Mayanna i in., 2015).

W glebach technogenicznych zawierających żużle hutnicze zidentyfikowano otoczki siarczanowe, które najprawdopodobniej powstały w wyniku uwalniania siarki podczas wietrzenia żużla. Jest to zgodne z badaniami dotyczącymi wietrzenia żużli hutniczych w warunkach środowiskowych (Kierczak i in., 2021). Chociaż żużle są materiałami antropogenicznymi (Warchulski i in., 2020), podlegają one naturalnym procesom wietrzenia podobnym do wietrzenia minerałów i skał (Kierczak i in., 2021). Ponadto wietrzenie żużli hutniczych skutkuje mobilizacją pierwiastków śladowych, takich jak Zn, Pb, Cu i As, które mogą stanowić zagrożenie dla lokalnego środowiska (Kierczak i in., 2013; Potysz i in., 2018).

W kilku badanych glebach, zwłaszcza tych o wyższej zawartości materii organicznej, zidentyfikowano oznaki aktywności biologicznej, w tym kanały powstałe dzięki aktywności fauny glebowej oraz korzeni, co jest zgodne z wynikami wcześniejszych badań (Arocena i in., 2010), które wskazują, że obecność materii organicznej sprzyja rozwojowi organizmów glebowych i intensyfikacji procesów bioturbacji. Ponadto, w żużlach znajdujących się w glebach z rejonu historycznego

hutnictwa stwierdzono występowanie przedstawicieli fauny (np. nicieni lub wazonkowców). Kolonizacja biologiczna obszarów poprzemysłowych, w tym składowisk odpadów przemysłowych, przyspiesza tworzenie się agregatów i różnicowanie struktury gleby (Santini i Fey, 2016; Domínguez-Haydar i in., 2018; Uzarowicz i in., 2020b) i stanowi dowód na kształtowanie się równowagi ekologicznej na obszarach przekształconych w wyniku historycznej działalności górniczej i hutniczej.

5.2.2. Selektywne ekstrakcje Fe, Al, Si i Mn jako chemiczne wskaźniki pedogenezy

Badania wykazały, że w glebach kwaśnych, zwłaszcza tych powstałych z odpadów górniczych zawierających skały magmowe i metamorficzne, procesy glebotwórcze prowadzą do mobilizacji Fe i Al. W glebach kwaśnych stwierdzono zwiększone zawartości form Fe i Al ekstrahowanych za pomocą szczawianu amonu, co jest charakterystyczne dla początkowych etapów wietrzenia chemicznego i zaawansowanych procesów glebotwórczych (np. bielicowania) (McKeague i Day, 1966; Krettek i Rennert, 2021). Uwalniania Fe i Al do roztworu glebowego, a następnie do wytrącania się amorficznych lub słabo krystalicznych tlenków i wodorotlenków jest prawdopodobnie skutkiem częściowego rozkładu pierwotnych glinokrzemianów (np. biotytu, muskowitu, plagioklazu) (Kalita i in., 2019). Podobne wyniki uzyskano w badaniach gleb technogenicznych w Polsce na historycznych hałdach kopalni miedzi w Miedzianej Górze i Miedziance (Uzarowicz i in., 2024), a także na hałdach kopalni rudy żelaza w rejonie Osicowej Góry (Uzarowicz i in., 2025), co potwierdza początek mobilizacji Fe i Al we wczesnych etapach pedogenezy.

W profilach 1 i 2 (grupa I gleb technogenicznych) wykryto bardzo wysokie zawartości Mn ekstrahowalnego za pomocą szczawianu amonu, co najprawdopodobniej wynika z wysokiej zawartości Mn w materiale macierzystym. Podwyższona zawartość Mn_{ox} w badanych glebach może wskazywać na aktywne procesy oksydo-redukcyjne i udział mikroorganizmów w utlenianiu Mn (Mayanna i in., 2015). Z kolei mobilizacja krzemu (Si_{ox}) jest związana z wietrzeniem pierwotnych minerałów zawierających Si i tworzeniem się wtórnych amorficznych form Si, które wydają się być typowe dla wczesnych etapów rozwoju gleb technogenicznych (Uzarowicz i in., 2024, 2025). Zawartości Al i Si ekstrahowalnego za pomocą szczawianu amonu były wyższe w glebach technogenicznych zawierających żużle hutnicze niż w innych badanych glebach. Cecha ta jest najprawdopodobniej związana z wietrzeniem żużli, któremu towarzyszy uwalnianie Al i Si z żużli. Uwalnianie Al i Si ekstrahowanych za pomocą szczawianu

amonu zostało udokumentowane jako efekt pedogenezy w glebach technogenicznych powstałych z popiołów i żużli z elektrowni węglowych (Uzarowicz i in., 2017), co odzwierciedla przemiany mineralne popiołów i żużli w środowisku glebowym.

Bardzo wysokie zawartości żelaza ekstrahowalnego za pomocą szczawianu amonu (Fe_{ox}) odnotowano w glebach technogenicznych zawierających żużle hutnicze, zwłaszcza tych zawierających żużle bogate w magnetyt (P11 i P12). Ilości Fe_{ox} w tych glebach są wyższe niż Fe_d, co jest sytuacją nietypową w środowisku glebowym. Podobne zjawisko zidentyfikowano w glebach technogenicznych powstałych z popiołów elektrowni cieplnych (Uzarowicz i in., 2017), gdzie wykazano, że wysoka zawartość Fe_{ox} nie zawsze odzwierciedla wyłącznie obecność pedogenicznych, amorficznych form Fe, ale może również być efektem obecności magnetytu. Jest to minerał, który ulega częściowemu rozpuszczeniu podczas ekstrakcji ditionitem i szczawianem (Walker, 1983; Fine i Singer, 1989; Van Oorschot i Dekkers, 1999). Dlatego też, gdy magnetyt występuje w glebie, trudno jest wyciągnąć wiarygodne wnioski na podstawie selektywnej ekstrakcji Fe.

5.3. Cechy geochemiczne i mobilność pierwiastków śladowych

5.3.1. Zanieczyszczenie badanych gleb na podstawie całkowitej zawartości pierwiastków śladowych w kontekście aktualnych przepisów prawnych w Polsce

Zawartość pierwiastków śladowych w analizowanych glebach została porównana z dopuszczalnymi zawartościami określonymi w polskich normach prawnych, które służą jako punkt odniesienia dla oceny zanieczyszczenia powierzchni ziemi w Polsce (Rozporządzenie Ministra Klimatu i Środowiska z 2024 r.). Dopuszczalne zawartości pierwiastków zostały przekroczone dla następujących metali (metaloidów): Cu (P5, P6, P8–P12), Zn (P12 – poziom 3C), Pb (P10, P12), Mo (P8), Hg (P5, P6, P8–P10, P12), As (P1, P2, P4–P12), Co (P1, P2, P8–P10, P12 – poziom 3C), Ni (P1, P2) i Ba (P1, P2, P4–P13). Zawartość Cu w glebach technogenicznych przekraczała dopuszczalne limity ponad 16-krotnie (P9), a Pb i Mo odpowiednio 1,2- i 2-krotnie. Dopuszczalne zawartości dla Hg zostały przekroczone 18-krotnie, a dla As 34-krotnie w tych glebach. Kobalt i Ni osiągnęły wartości odpowiednio 6- i 4-krotnie wyższe od określonych w polskich przepisach. Bar osiągnął wartości 160-krotnie wyższe od wartości dopuszczalnych. W poziomie 3C profilu 12, która najprawdopodobniej jest warstwą zawierającą pozostałości rudy polimetalicznej o wysokich zawartościach pierwiastków śladowych, przekroczono

dopuszczalne zawartości Cu (66-krotnie), Zn (1,4-krotnie), Pb (1,7-krotnie), Hg (16-krotnie), As (45-krotnie), Co (2,5-krotnie) i Ba (7,5-krotnie). Natomiast zawartości Cr, Cd i Sn we wszystkich badanych glebach nie przekroczyły dopuszczalnych limitów.

5.3.2. Ocena mobilności pierwiastków śladowych w badanych glebach na podstawie sekwencyjnej ekstrakcji metodą BCR

Dzięki czterostopniowej analizie BCR zidentyfikowano formy pierwiastków w celu oceny ich mobilności (Art. 3: Ryc. 3–5, Tabela 3). W kontekście potencjalnego wpływu pierwiastków śladowych na środowisko najważniejsze jest określenie zawartości tych pierwiastków w pierwszej frakcji (F1), tj. w najbardziej mobilnych formach w glebie. W grupie II gleb technogenicznych (P9 i P10) stwierdzono wysoką zawartość Cu sięgającą nawet 174 $mg \cdot kg^{-1}$ (poziom C1, P10) w F1. Stosunkowo wysokie zawartości Cu i Sb (odpowiednio 43 i 7 $mg \cdot kg^{-1}$) odnotowano w poziomie 3C profilu 12, który był warstwą skał rudonośnych zachowanych w profilu glebowym na obszarze historycznego hutnictwa. Najwyższa zawartość Zn w F1 została zmierzona w profilu w Kuźnicach (P13) i wyniosła 50 $mg \cdot kg^{-1}$ (poziom AC). W innych lokalizacjach zawartość Zn osiągnęła maksymalnie 9 $mg \cdot kg^{-1}$ (P3, poziom O/C) lub około 3–4 $mg \cdot kg^{-1}$ (P6, poziomy Bw i C). Zawartość Pb w F1 wynosiła do 0,9 $mg \cdot kg^{-1}$ (P11, poziom A), As do 1,2 $mg \cdot kg^{-1}$ (P3, poziom O/C), Co do 1,1 $mg \cdot kg^{-1}$ (P9, poziom AC), Ni i Cd do 0,3 $mg \cdot kg^{-1}$, Cr do 0,9 $mg \cdot kg^{-1}$, Sr do 58 $mg \cdot kg^{-1}$, Ba do 213 $mg \cdot kg^{-1}$ i Mn do 2242 $mg \cdot kg^{-1}$ (P13, poziom AC).

Uzyskane wyniki wskazują na potencjalną mobilność głównie Cu, Zn, Mn, Ba, Sr, co może stanowić zagrożenie dla środowiska poprzez możliwe pobieranie pierwiastków śladowych przez rośliny i ich wymywanie do wód gruntowych i powierzchniowych, w tym strumieni górskich występujących zazwyczaj w pobliżu składowisk odpadów, sztolni, szybów i historycznych obszarów hutniczych. Takie obserwacje są zgodne z wynikami wcześniejszych badań, które podkreślają znaczenie pierwszych frakcji w sekwencyjnych ekstrakcjach jako kluczowego wskaźnika zawartości metali biodostępnych i mobilnych w zanieczyszczonych glebach (Kodirov i in., 2018; Kicińska i in., 2022; Swęd i in., 2022; Uzarowicz i in., 2024).

5.3.3. Cechy geochemiczne gleb technogenicznych na podstawie całkowitych zawartości pierwiastków śladowych i pierwiastków ziem rzadkich

Grupa I gleb technogenicznych (w szczególności P1 i P2), powstałych z odpadów górniczych zawierających skały węglanowe, charakteryzowała się podwyższonymi

zawartościami pierwiastków syderofilnych (Co i Ni), a także Fe i Mn, co odzwierciedlało geogeniczne pochodzenie tych pierwiastków ze skał zawierających rozproszone rudy Fe i Mn. Gleby technogeniczne z grupy I charakteryzowały się również stosunkowo wysoką (w porównaniu z innymi glebami) sumą pierwiastków ziem rzadkich (do 786 $mg \cdot kg^{-1}$), co najprawdopodobniej wynikało z dużej zawartości minerałów zawierających pierwiastki ziem rzadkich oraz silnego powinowactwa pierwiastków ziem rzadkich do minerałów węglanowych w skałach (Liang i in., 2014).

Gleby technogeniczne z grupy II (P5–P10), powstałe z odpadów górniczych stanowiących skały magmowe i metamorficzne zawierających pozostałości rud polimetalicznych, wykazywały bardzo dużą zmienność zawartości pierwiastków śladowych, ze znacznym wzbogaceniem w pierwiastki chalkofilne (Cu, Mo, Hg, As, Sb i Bi), ale także Ba, Sr, U i Th. Cechy te odzwierciedlały polimetaliczny charakter rud rozproszonych w skałach macierzystych. Niższa suma pierwiastków ziem rzadkich (do 346 $mg \cdot kg^{-1}$) w porównaniu z glebami z grupy I sugerowała najprawdopodobniej mniejszą zawartość minerałów zawierających pierwiastki ziem rzadkich w materiale macierzystym.

Grupa III gleb technogenicznych (P11–P13), zawierająca żużle hutnicze, wykazywała najbardziej zróżnicowane zawartości pierwiastków śladowych. Wyłączając poziom 3C w profilu 12 (ponieważ najprawdopodobniej była to warstwa skał rudonośnych zachowanych w profilu glebowym), należy stwierdzić, że gleby te były wzbogacone w szereg metali (Cu, As, Sb, Ba, Hg, Co i Ag) pochodzących z rud przetwarzanych w hutach, które były w większości reprezentowane przez rudy polimetaliczne. Stosunkowo niska suma pierwiastków ziem rzadkich (<237 $mg \cdot kg^{-1}$) była również cechą charakterystyczną gleb technogenicznych z grupy III.

5.3.4. Związek między frakcjonowaniem pierwiastków a właściwościami gleb

Zależność między pH a zawartością pierwiastków w frakcjach (F1–F4) wykazała ujemną korelację między pH gleb a zawartością Cu, Zn, Pb, Sb, Ba, Co i Mn w F1, która jest frakcją najbardziej mobilną. Wskazuje to, że im niższe pH gleby, tym wyższa zawartość wyżej wymienionych pierwiastków w F1. Dlatego też w glebach kwaśnych należy spodziewać się najwyższej mobilności Cu, Zn, Pb, Sb, Ba, Co i Mn. Z drugiej strony, korelacje między pH gleby a zawartością As i Sr w F1 były dodatnie, co wskazywało, że im wyższe pH (w zakresie pH występującym w badanych glebach), tym wyższa mobilność As i Sr w badanych glebach.

Analizy statystyczne wykazały istotną ujemną korelację między zawartością węglanów w glebach a zawartością Cu, Zn, Pb, Sb, Ba, Co i Mn w F1. Wyniki te wykazały, że obecność węglanów w glebie zmniejszała mobilność wyżej wymienionych pierwiastków. Wynik ten odzwierciedla wspomnianą powyżej korelację między zawartością pierwiastków a pH.

Analizy statystyczne wykazały również istotne dodatnie korelacje między zawartością TOC a zawartościami Zn, Pb i Cr w F3, który uznawana jest za frakcję związaną z glebową materią organiczną. Wyniki te wykazały, że wyżej wymienione pierwiastki wykazywały wysokie powinowactwo do glebowej materii organicznej. Z kolei As był pierwiastkiem niezwiązanym z materią organiczną w badanych glebach technogenicznych, co potwierdzała ujemna korelacja między zawartością TOC a zawartością As w F3. Wyniki te były zgodne z wynikami innych autorów (Romero-Freire i in., 2014; Hattab i in., 2015; Paniagua-López i in., 2023).

6. Wnioski

1. Najważniejszymi czynnikami glebotwórczymi kontrolującymi genezę i właściwości gleb technogenicznych były: dawna działalność przemysłowa człowieka, rodzaj materiału macierzystego i roślinność. Czynniki antropogeniczne związane z działalnością górniczą i hutniczą miały bezpośredni i decydujący wpływ na genezą badanych gleb technogenicznych. Materiał macierzysty determinował większość właściwości gleby (pH, zawartość węglanów, właściwości sorpcyjne), podatność magnetyczną, a także skład mineralny i chemiczny. Roślinność wpływała na właściwości wierzchniej warstwy gleby, np. poprzez akumulację materii organicznej.
2. Mimo początkowego stadium rozwoju, w badanych glebach zidentyfikowano mikromorfologiczne i submikromorfologiczne przejawy procesów glebotwórczych, z których najważniejszymi były: (1) pseudomorfozy tlenku żelaza w wyniku wietrzenia siarczków; (2) pedogeniczna struktura w powierzchniowych poziomach glebowych; (3) pedogeniczne otoczki oraz (4) bioturbacje.
3. Na rozwój struktury gleby w badanych glebach technogenicznych wpływ ma obecność węglanów, akumulacja materii organicznej w wierzchniej warstwie gleby, a także penetracja korzeni i bioturbacja spowodowana aktywnością fauny.
4. Otoczki pedogeniczne występujące w badanych glebach technogenicznych odzwierciedlają właściwości geochemiczne materiałów macierzystych. W glebach powstałych z odpadów górniczych zawierających węglany występowały otoczki z wtórnych węglanów wapnia. W kwaśnych glebach pochodzących z odpadów górniczych zawierających glinokrzemiany otoczki tlenku żelaza były powszechne w poziomach Bw, natomiast otoczki tlenku manganu występowały sporadycznie. W glebach zawierających żużle hutnicze stwierdzono otoczki siarczanowe, najprawdopodobniej powstałe w wyniku wietrzenia żużli i uwalniania się siarki do środowiska glebowego.
5. W większości badanych gleb technogenicznych zaobserwowano bioturbacje takie jak kanały korzeniowe i kanały biogeniczne wypełnione materiałem przetworzonym przez zwierzęta glebowe. Zwierzęta glebowe (najprawdopodobniej nicienie lub wazonkowce) znaleziono w przestrzeniach wewnątrz fragmentów żużli występujących w glebach w rejonach danego hutnictwa.
6. Metody selektywnej ekstrakcji wykazały uwalnianie Mn ekstrahowalnego za pomocą roztworu szczawianu amonu w glebach powstałych z odpadów górniczych

zawierających Mn, niewielką mobilizację Fe i Al ekstrahowalnego za pomocą roztworu szczawianu amonu w kwaśnych glebach powstałych z materiału macierzystego zawierającego glinokrzemiany oraz uwalnianie Al i Si ekstrahowalnego za pomocą roztworu szczawianu amonu w utworach glebowych zawierających żużle hutnicze. Obecność Fe, Al, Mn i Si ekstrahowalnego za pomocą roztworu szczawianu amonu w badanych glebach jest efektem działania procesów wietrzenia mineralnego substratu glebowego.

7. Badane gleby technogeniczne w Tatrach wykazują znaczne zanieczyszczenie niektórymi pierwiastkami śladowymi przekraczającymi dopuszczalne zawartości dla Cu, Zn, Pb, Mo, Hg, As, Co, Ni i Ba zgodnie z aktualnymi przepisami prawnymi obowiązującymi w Polsce.
8. Czterostopniowa sekwencyjna analiza metodą BCR pozwoliła na identyfikację pierwiastków śladowych w najbardziej mobilnych formach (F1). W F1 w określonych poziomach niektórych gleb stwierdzono wysoką zawartość Cu, Zn, Sb, Pb, As, Co, Ni, Cd, Cr, Sr, Ba i Mn, co wskazuje, że pierwiastki te mogą wykazywać wysoką mobilność w badanych glebach. Podkreśla to potencjalne zagrożenia dla środowiska związane z obecnością pierwiastków śladowych, wynikające z możliwości pobierania tych pierwiastków przez rośliny oraz przedostawania się ich do wód gruntowych i powierzchniowych.
9. Badania wykazały zależności między formami pierwiastków a właściwościami gleb, takimi jak pH, obecność węglanów i zawartość glebowej materii organicznej. Analizy statystyczne wykazały wzrost mobilności Cu, Zn, Pb, Sb, Ba, Co i Mn wraz ze spadkiem pH gleby i spadkiem zawartości węglanów. Jednak zachowanie As i Sr wykazywało odwrotną tendencję: im wyższe pH, tym większa mobilność tych pierwiastków. Wyniki wykazały pozytywne korelacje między zawartościami Zn, Pb i Cr a zawartościami TOC.

7. Literatura

1. Allory, V., Séré, G., Ouvrard, S., 2022. A meta-analysis of carbon content and stocks in Technosols and identification of the main governing factors. European Journal of Soil Science 73(1), e13141. https://doi.org/10.1111/ejss.13141
2. Arocena, J., Mourik, J.M., Schilder, M., Faz Cano, A., 2010. Initial soil development under pioneer plant species in metal mine waste deposits. Restoration Ecology 18, 244–252. https://doi.org/10.1111/j.1526-100X.2009.00582.x
3. Badin, A.L., Méderel, G., Béchet, B., Borschneck, D., Delolme, C., 2009. Study of the aggregation of the surface layer of Technosols from stormwater infiltration basins using grain size analyses with laser diffractometry. Geoderma 153, 163–171. https://doi.org/10.1016/j.geoderma.2009.07.022
4. Brogowski, Z., Czerwiński, Z., 2016. Materiały do ćwiczeń z gleboznawstwa. Część II. Wydawnictwo SGGW, Warszawa. (in Polish)
5. Castillo Corzo, M., Peña Rodríguez, V., Manrique Nugent, M., Villarreyes Peña, E., Byrne, P., Gonzalez, J.C., Patiño Camargo, G., Barnes, C.H.W., Sánchez Ortiz, J.F., Saldaña Tovar, J., De Los Santos Valladares, L., 2025. Potentially toxic elements and radionuclides contamination in soils from the vicinity of an ancient mercury mine in Huancavelica, Peru. Soil Science Annual 76(2), 204389. https://doi.org/10.37501/soilsa/204389
6. Charzyński, P., Hulisz, P., Bednarek, R.M. (Eds.), 2013. Technogenic soils of Poland. Torun, Polish Society of Soil Science.
7. Ciarkowska, K., Miechówka, A., 2022. Identification of the factors determining the concentration and spatial distribution of Zn, Pb and Cd in the soils of the non-forest Tatra Mountains (southern Poland). Environmental Geochemistry and Health 44, 4323–4341. https://doi.org/10.1007/S10653-022-01201-3
8. Colombini, G., Auclerc, A., Watteau, F., 2020. Techno-moder: A proposal for a new morpho-functional humus form developing on Technosols revealed by micromorphology. Geoderma 375, 114526. https://doi.org/10.1016/j.geoderma.2020.114526
9. Cornell, R.M., Schwertmann, U., 2003. The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, Second Edition. Wiley-VCH Verlag.
10. Demková, L., Bobuľská, L., Árvay, J., Homolová, Z., Michalko, M., Bálintová, M., 2023. Potentially toxic elements in soil and air along an altitudinal gradient in Tatra National Park. Journal of Geochemical Exploration 252, 107268. https://doi.org/10.1016/j.gexplo.2023.107268.
11. Díaz-Ortega, J., Rivera-Uria, Y., López-Mendoza, E., Sedov, S., Romero, F., Solleiro-Rebolledo, E., Martínez-Jardines, L.G., 2024. Development of sustainable hydromorphic Technosols within artificial wetlands in mining landscapes: the effects of wastewater and hydrothermal geological materials. Journal of Soils and Sediments 24, 2948–2962. https://doi.org/10.1007/s11368-024-03763-4
12. Domínguez-Haydar, Y., Castañeda, C., Rodríguez-Ochoa, R., Jiménez, J.J., 2018. Assessment of soil fauna footprints at a rehabilitated coal mine using micromorphology and near infrared spectroscopy (NIRS). Geoderma 313, 135–145. https://doi.org/10.1016/j.geoderma.2017.10.032
13. Drewnik, M., 2002. Rate of organic matter decomposition and humus horizons in the Tatra soils. In: Changes of the nature environment of the Tatra Mountains (Ed. Borowiec, W., Kotarba A., Kownacki, A., Krzan, Z., Mirek, Z.). Kraków, Polskie Towarzystwo Przyjaciół Nauk o Ziemi, p. 101–106.

14. Drewnik, M., 2006. The effect of environmental conditions on the decomposition rate of cellulose in mountain soils. Geoderma 132, 116–130. https://doi.org/10.1016/j.geoderma.2005.04.023
15. Drewnik, M., 2008. Geomorfologiczne uwarunkowania rozwoju pokrywy glebowej w obszarach górskich na przykładzie Tatr. Wydawnictwo UJ.
16. Eren, M., Kadir, S., Zucca, C., Akşit, İ., Kaya, Z., Kapur, S., 2014. Pedogenic manganese oxide coatings (calcium buserite) on fracture surfaces in Tortonian (Upper Miocene) red mudstones, southern Turkey. Catena 116, 149–156. https://doi.org/10.1016/j.catena.2014.01.003
17. Eswaran, H., Raghu Mohan, G., 1973. The microfabric of petroplinthite. Soil Science Society of America Proceedings 37, 79–82. https://doi.org/10.2136/sssaj1973.03615995003700010027x
18. Fine, P., Singer, M.J., 1989. Contribution of ferrimagnetic minerals to oxalate- and dithionite-extractable iron. Soil Science Society of America Journal 53, 191–196.
19. Gradziński, M., Jach, R., Stworzewicz, E., 2001. Origin of calcite-cemented Holocene slope breccias from the Długa Valley (the Western Tatra Mountains). Annales Societatis Geologorum Poloniae 71(2), 105–113.
20. Grünewald, G., Kaiser, K., Jahn, R., 2007. Alteration of secondary minerals along a time series in young alkaline soils derived from carbonatic wastes of soda production. Catena 71(3), 487–496. https://doi.org/10.1016/j.catena.2007.03.022
21. Hattab, N., Motelica-Heino, M., Faure, O., Bouchardon, J.L., 2015. Effect of fresh and mature organic amendments on the phytore-mediation of technosols contaminated with high concentrations of trace elements. Journal of Environmental Management 159, 37–47. https://doi.org/10.1016/j.jenvman.2015.05.012.
22. Hayes, S.M., Root, R.A., Perdrial, N., Maier, R.M., Chorover, J., 2014. Surficial weathering of iron sulfide mine tailings under semi-arid climate. Geochimica et Cosmochimica Acta 141, 240–257. https://doi.org/10.1016/j.gca.2014.05.030
23. Hedde, M., Nahmani, J., Séré, G., Auclerc, A., Cortet, J., 2019. Early colonization of constructed Technosols by macro-invertebrates. Journal of Soils and Sediments 19, 3193–3203. https://doi.org/10.1007/s11368-018-2142-9
24. Hess, M., 1996. Climate. [In:] Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Nature of the Tatra National Park. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 53–68.
25. Huot, H., Simonnot, M.O., Morel, J.L., 2015. Pedogenetic trends in soils formed in technogenic parent materials. Soil Science 180(4/5), 182–192. https://doi.org/10.1097/SS.0000000000000135
26. Huot, H., Simonnot, M.O., Watteau, F., Marion, P., Yvon, J., De Donato, P., Morel, J.L., 2014. Early transformation and transfer processes in a Technosol developing on iron industry deposits. European Journal of Soil Science 65, 470–484. https://doi.org/10.1111/ejss.12106
27. IUSS Working Group WRB, 2022. World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps. 4th edition. International Union of Soil Sciences (IUSS), Vienna, Austria.
28. Jangorzo, N.S., Schwartz, C., Watteau, F., 2014. Image analysis of soil thin sections for a non-destructive quantification of aggregation in the early stages of pedogenesis. European Journal of Soil Science 65(4), 485–498. https://doi.org/10.1111/ejss.12110
29. Jangorzo, N.S., Watteau, F., Schwartz, C., 2013. Evolution of the pore structure of constructed Technosol during early pedogenesis quantified by image analysis. Geoderma 207–208, 180–192. https://doi.org/10.1016/j.geoderma.2013.05.016
30. Jost, H., 2004. Dzieje górnictwa i hutnictwa w Tatrach Polskich. Zakopane. (in Polish)

31. Kabała, C., Greinert, A., Charzyński, P., Uzarowicz, Ł., 2020. Technogenic soils – soils of the year 2020 in Poland. Concept, properties and classification of technogenic soils in Poland. Soil Science Annual 71(4), 267–280. https://doi.org/10.37501/soilsa/131609
32. Kalita, P., Dutta, M., Karmakar, R. M., Dutta, S., Deka, B., 2019. Pedogenic distribution of iron and aluminium under different land uses in Golaghat district of Assam. Journal of Pharmacognosy and Phytochemistry 8(3), 2554–2561.
33. Kicińska, A., Pomykała, R., Izquierdo-Diaz, M., 2022. Changes in soil pH and mobility of heavy metals in contaminated soils. European Journal of Soil Science 73, e13203. https://doi.org/10.1111/ejss.13203.
34. Kierczak, J., Pietranik, A., Piatak, N.M. 2021. Weathering of Slags. [In:] Piatak N.M., Ettler, V. (Eds.), Metallurgical Slags: Environmental Geochemistry and Resource Potential, The Royal Society of Chemistry, pp. 125–150.
35. Kierczak, J., Potysz, A., Pietranik, A., Tyszka, R., Modelska, M., Néel, C., Ettler, V., Mihaljevič, M., 2013. Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland). Journal of Geochemical Exploration 124, 183–194. https://doi.org/10.1016/j.gexplo.2012.09.008
36. Klimaszewski, M., 1996. Geomorphology. [In:] Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Nature of the Tatra National Park. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 97–124.
37. Kodirov, O., Kersten, M., Shukurov, N., Peinado, F.J.M., 2018. Trace metal (loid) mobility in waste deposits and soils around Chadak mining area, Uzbekistan. Science of The Total Environment 622, 1658–1667. https://doi.org/10.1016/j.scitotenv.2017.10.049.
38. Komornicki, T., Skiba, S., 1996. Gleby, in: Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Przyroda Tatrzańskiego Parku Narodowego. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 215–229.
39. Konstantinov, A., Novoselov, A., Konstantinova, E., Loiko, S., Kurasova, A., Minkina, T., 2020. Composition and properties of soils developed within the ash disposal areas originated from peat combustion (Tyumen, Russia). Soil Science Annual 71(1), 3–14. https://doi.org/10.37501/soilsa/121487
40. Korzeniowska, J., Krąż, P., 2020. Heavy Metals Content in the Soils of the Tatra National Park Near Lake Morskie Oko and Kasprowy Wierch—A Case Study (Tatra Mts, Central Europe). Minerals 10, 1120. https://doi.org/10.3390/min10121120
41. Kowalska, J.B., Gąsiorek, M., Zadrożny, P., Nicia, P., Waroszewski, J., 2021. Deep subsoil storage of trace elements and pollution assessment in mountain Podzols (Tatra Mts., Poland). Forests 12, 291. https://doi.org/10.3390/f12030291.
42. Kowalska, J.B., Zaleski, T., Mazurek, R., 2020. Micromorphological features of soils formed on calcium carbonate-rich slope deposits in the Polish Carpathians. Journal of Mountain Science 17(6), 1310–1332. https://doi.org/10.1007/s11629-019-5829-5
43. Kotański, Z., 1971. Przewodnik geologiczny po Tatrach. Wydawnictwo Geologiczne, Warszawa. (in Polish)
44. Krettek, A., Rennert, T., 2021. Mobilisation of Al, Fe, and DOM from topsoil during simulated early Podzol development and subsequent DOM adsorption on model minerals. Scientific Reports 11, 19741. https://doi.org/10.1038/s41598-021-99365-y\
45. Kubica, B., Kwiatek, W.M., Stobiński, M., Skiba, S., Skiba, M., Gołaś, J., Kubica, M., Tuleja-Krysa, M., Wrona, A., Misiak, R., Krzan, Z., 2007. Concentrations of 137Cs, 40K radionuclides and some heavy metals in soil samples of Chochołowska Valley from Tatra National Park. Polish Journal of Environmental Studies 16, 723–729.
46. Kubica, B., Mietelski, J.W., Gołaś, J., Skiba, S., Tomankiewicz, E., Gaca, P., Jasińska, M., Tuleja-Krysa, M., 2002. Concentration of 137 Cs, 40 K, 238 Pu and 239+240 Pu Radionuclides and Some Heavy Metals in Soil Samples from Two Main Valleys from Tatra National Park. Polish Journal of Environmental Studies 11, 537–545.

47. Kuligiewicz, A., Szymański, W., Bindeman, I., Kowalik-Hyla, M., Ciesielska, Z., Ziemiański, P. P., Różański, K., 2024a. Links between environmental conditions and pedogenic phyllosilicates in Podzols in the Tatra Mountains (Poland)–I. Mineralogy. Geoderma, 449, 116981. https://doi.org/10.1016/j.geoderma.2024.116981
48. Kuligiewicz, A., Bindeman, I., Szymański, W., Różański, K., Salata, D., 2024b. Links between environmental conditions and pedogenic phyllosilicates in Podzols in the Tatra Mountains (Poland)–II. Hydrogen and oxygen isotope compositions. Geoderma, 449, 116985. https://doi.org/10.1016/j.geoderma.2024.116985
49. Kwapuliński, J., Paprotny, L., Paukszto, A., Kowol, J., Rochel, R., Nogaj, E., Musielińska, R., Celinski, R., 2013. Influence of the type of tree habitat on the character of co-occurrence of Fe, Mn, Zn, Cu, Pb, Ni, Cr and Co in the soil of the Tatra Mountain National Park. Annals of Agricultural and Environmental Medicine 20, 494–499.
50. Kwapuliński, J., Paukszto, A., Paprotny, Ł., Musielińska, R., Kowol, J., Nogaj, E., Rochel, R., 2012. Bioavailability of Lead, Cadmium, and Nickel in Tatra Mountain National Park Soil. Polish Journal of Environmental Studies 21, 407–413.
51. Liang, T., Li, K., Wang, L., 2014. State of rare earth elements in different environmental components in mining areas of China. Environmental Monitoring and Assessment 186, 1499–1513. https://doi.org/10.1007/s10661-013-3469-8.
52. Mayanna, S., Peacock, C.L., Schäffner, F., Grawundera, A., Mertena, D., Kothec, E., Büchela, G., 2015. Biogenic precipitation of manganese oxides and enrichment of heavy metals at acidic soil pH. Chemical Geology 402, 6–17. https://doi.org/10.1016/j.chemgeo.2015.02.029
53. McKeague, J.A., Day, J.H., 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Canadian Journal of Soil Science 46(1), 13–22. https://doi.org/10.4141/cjss66-003
54. McKenzie, R.M. 1989. Manganese oxides and hydroxides. [In:] Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments, Soil Science Society of America. Madison, WI, pp. 439–461.
55. Mehra, O.P., Jackson, M.L., 1958. Iron oxide removal from soils and clay by a dithionite-citrate system buffered with sodium bicarbonate. Clays and Clay Minerals 7, 317–327. https://doi.org/10.1346/CCMN.1958.0070122
56. Miechówka, A., 1989. Geochemical characteristics of Tatra rendzinas formed on dolomites. Cz. I. Ogólna charakterystyka gleb i niektóre dane mineralogiczne. Soil Science Annual 40, 83–105.
57. Miechówka, A., 2001. Zawartość różnych form żelaza w rędzinach położonych powyżej górnej granicy lasu w Tatrach. Soil Science Annual 52, 135–143.
58. Miechówka, A., Ciarkowska, K., 1998. Mikromorfologiczne formy próchnicy tatrzańskich rędzin próchnicznych i butwinowych. Zeszyty Problemowe Postępów Nauk Rolniczych 464, 161–168.
59. Miechówka, A., Gasiorek, M., Zaleski, T., 1997. Contents of cadmium and nickel in the soils and plants of grazed mountain glades in Tatra National Park. Zeszyty Problemowe Postępów Nauk Rolniczych, 448, 197–202.
60. Miechówka, A., Niemyska-Łukaszuk, J., 2004. Content diversity of Zn, Pb and Cd in Lithic Leptosols of the Tatra National Park (Poland). Oecologia Montana 13, 1–5.
61. Miechówka, A., Niemyska-Łukaszuk, J., Ciarkowska, K., 2002a. Heavy metals in selected non-forest soils from the Tatra National Park. Chemia i Inżynieria Ekologiczna 9, 1433–1438.
62. Miechowka, A., Niemyska-Lukaszuk, J., Gasiorek, M., 2002b. Content of Zn, Pb, Cd and Ni in peat-bog and fen soils in the Tatra National Park. Acta Agrophysica, 67.
63. Miechówka, A., Zadrozny, P., Mazurek, R., Ciarkowska, K., 2021. Classification of mountain non-forest soils with umbric horizon - a case study from the Tatra Mountains (Poland). Soil Science Annual 72, 134619. https://doi.org/10.37501/soilsa/134619

64. Mossop, K.F., Davidson, C.M., 2003. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. Analytica Chimica Acta 478, 111–118. https://doi.org/10.1016/S0003-2670(02)01485-X
65. Néel, C., Bril, H., Courtin-Nomade, A., Dutreuil, J.P., 2003. Factors affecting natural development of soil on 35-year-old sulphide-rich mine tailings. Geoderma 111, 1–20. https://doi.org/10.1016/S0016-7061(02)00237-9
66. Niemyska-Łukaszuk, J., 1977. Characteristics of the humus of some forest soils in the Tatra Mts. Part. II. Fractionary composition of the humus compounds. Soil Science Annual 28, 143–168.
67. Oleksynowa, K., Skiba, S., 1977. Characteristics of some cryogenic soils in the Tatra Mts. Soil Science Annual 28, 293–312.
68. Oleksynowa, K., Skiba, S., Kania, W., 1977. Introductory investigations on the geochemistry of rendzinas in the Tatra Mts. Soil Science Annual 28, 263–275.
69. Ortega, J., Sedov, S., Romero, F., Jardines, L., Solleiro-Rebolledo, E., 2022. Chronosequence of Technosols at the Peña Colorada mine in Colima, Mexico: a short-term remediation alternative. Journal of Soils and Sediments 22, 942–956. https://doi.org/10.1007/s11368-021-02990-3
70. Ostrowska, A., Gawliński, S., Szczubiałka, Z., 1991. Metody analizy i oceny właściwości gleb i roślin. Instytut Ochrony Środowiska, Warszawa.
71. Paniagua-López, M., Aguilar-Garrido, A., Contero-Hurtado, J., García-Romera, I., Sierra-Aragón, M., Romero-Freire, A., 2023. Eco-toxicological assessment of polluted soils one year after the application of different soil remediation techniques. Toxics 11, 298. https://doi.org/10.3390/toxics11040298.
72. Pansu, M., Gautheyrou, J., 2006. Handbook of Soil Analysis. Mineralogical, Organic and Inorganic Methods. Springer Berlin, Heidelberg.
73. Paprotny, Ł., Kwapuliński, J., Wianowska, D., Gnatowski, M., Kasprzyk-Pochopień, J., Piekoszewski, W., 2024. A Comparison of Co-Occurrence of Special Forms of Selected Metals in Soil, on the Example of Sycamore, Beech, and Spruce Forest Complexes in Urbanized and Non-Urbanized Regions of Tatra National Park. Polish Journal of Environmental Studies 33, 4273–4282. https://doi.org/10.15244/pjoes/177422
74. Paukszto, A., Mirosławski, J., 2019. Using stinging nettle (*Urtica dioica* L.) to assess the influence of long-term emission upon pollution with metals of the Tatra National Park area (Poland). Atmospheric Pollution Research 10, 73–79. https://doi.org/10.1016/j.apr.2018.06.004.
75. Piękoś-Mirkowa, H., Mirek, Z., 1996. Zbiorowiska roślinne, in: Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Przyroda Tatrzańskiego Parku Narodowego. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 237–274.
76. Potysz, A., Kierczak, J., Grybos, M., Pędziwiatr, A., van Hullebusch, E.D., 2018. Weathering of historical copper slags in dynamic experimental system with rhizosphere-like organic acids. Journal of Environmental Management 222, 325–337. https://doi.org/10.1016/j.jenvman.2018.05.071
77. Radwańska-Paryska, Z., Paryski, W.H., 1995. Wielka Encyklopedia Tatrzańska. Wyd. Górskie, Poronin, pp. 1555.
78. Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P., 1999. Improvement of the BCR three-step sequential extraction procedure prior to the certification of new sediment and soil reference materials. Journal of environmental monitoring 1, 57–61. https://doi.org/10.1039/A807854H
79. Rączkowska, Z.J., 2019. Human impact in the Tatra Mountains. Cuadernos de investigación geográfica / Geographical Research Letters 45(1), 219–244.

80. Romero-Freire, A., Sierra-Aragón, M., Ortiz-Bernad, I., Martín-Peinado, F.J., 2014. Toxicity of arsenic in relation to soil properties: Implications to regulatory purposes. Journal of Soils and Sediments 14, 968–979. https://doi.org/10.1007/s11368-014-0845-0
81. Rozporządzenie Ministra Klimatu i Środowiska z 2024 r. Rozporządzenie Ministra Klimatu i Środowiska z dnia 31 października 2024 r. zmieniające rozporządzenie w sprawie sposobu prowadzenia oceny zanieczyszczenia powierzchni ziemi Dz.U. 2024 poz. 1657. Dostępne online: https://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20240001657 (dostęp 16 września 2025 r.)
82. Ruiz, F., Andrade, G.R.P., Sartor, L.R., Santos, J.C.B. dos, Souza Júnior, V.S. de, Ferreira, T.O., 2022. The rhizosphere of tropical grasses as driver of soil weathering in embryonic Technosols (SE-Brazil). Catena 208, 105764. https://doi.org/10.1016/j.catena.2021.105764
83. Santini, T.C., Fey, M.V., 2016. Assessment of Technosol formation and in situ remediation in capped alkaline tailings. Catena 136, 17–29. https://doi.org/10.1016/j.catena.2015.08.006
84. Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung. Zeitschrift für Pflanzenernährung und Bodenkunde 105, 194–202.
85. Séré, G., Schwartz, C., Ouvrard, S., Renat, J.C., Watteau, F., Villemin, G., Morel, J.L., 2010. Early pedogenic evolution of constructed Technosols. Journal of Soils and Sediments 10, 1246–1254. https://doi.org/10.1007/s11368-010-0206-6
86. Skiba, S., 1977. Studies on mountain soils formed in various phytoclimatic zones of the crystalline part of the Polish Tatra Mts. Soil Science Annual 28(1), 205–241.
87. Skiba, S., 1983. Tendencies towards zonality in the rendzinas of the Tatra Mts. (with the soils of the slope of Mt. Kominiarski Wierch as an example). Soil Science Annual 34, 101–112.
88. Skiba, S., 1985. Rola klimatu i roślinności w genezie gleb na przykładzie gleb górskich z Tatr Polskich i z gór Mongolii. Zeszyty Naukowe Akademii Rolniczej w Krakowie, seria Rozprawy Habilitacyjne 99, 1–72.
89. Skiba, M., 2007. Clay mineral formation during podzolization in an alpine environment of the Tatra Mountains, Poland. Clays and Clay Minerals 55, 618–634. https://doi.org/10.1346/CCMN.2007.0550609
90. Skiba, S., Drewnik, M., Klimek, M., Kacprzak, A., Żyła, M., 2004. Soil cover in the Carpathian national parks in Poland. Przyroda Człowiek Bóg 1, 115–125.
91. Skiba, M., Szczerba, M., Skiba, S., Bish, D.L., Grybos, M., 2011. The nature of interlayering in clays from a podzol (Spodosol) from the Tatra Mountains, Poland. Geoderma 160, 425–433. https://doi.org/10.1016/j.geoderma.2010.10.013
92. Soil Science Division Staff, 2017. Soil Survey Manual. Ditzler, C., Scheffe, K., Monger H.C. (Eds.) USDA Handbook 18. Washington, D.C.
93. Staszewski, T., Łukasik, W., Kubiesa, P., 2012. Contamination of Polish national parks with heavy metals. Environmental Monitoring and Assessment 184, 4597–4608.
94. Stobiński, M., Kubica, B., 2017. Chemometric analysis of 137Cs activity and heavy metals distribution in the Tatras' soil. International Journal of Environmental Science and Technology 14, 1217–1224. https://doi.org/10.1007/s13762-016-1225-7.
95. Stolarczyk, M., Musielok, Ł., Szymański, W., Drewnik, M., 2024. Morphology, properties and classification of folisols in the Tatra Mountains. Soil Science Annual 75(4), 195239. https://doi.org/10.37501/soilsa/195239
96. Stoops, G., 2021. Guidelines for analysis and description of soil and regolith thin sections. John Wiley & Sons, 184 p.

97. Stoops, G., Marcelino, V., Mees, F., 2018. Micromorphological features and their relation to processes and classification: general guidelines and Overview. [In:] Stoops, G., Marcelino, V., Mees, F. (Eds.), Interpretation of Micromorphological Features of Soils and Regoliths. Elsevier, pp. 15–35.
98. Strzemski, M., 1956. Gleby Tatr Polskich. Soil Science Annual 5, 3–71.
99. Sullivan, L.A., Koppi, A.J., 1992. Manganese oxide accumulations associated with some soil structural pores. I. Morphology, composition and genesis. Australian Journal of Soil Research 30(4), 409–427. https://doi.org/10.1071/SR9920409
100. Swęd, M., Uzarowicz, Ł., Duczmal-Czernikiewicz, A., Kwasowski, W., Pędziwiatr, A., Siepak, M., Niedzielski, P., 2022. Forms of metal (loid) s in soils derived from historical calamine mining waste and tailings of the Olkusz Zn–Pb ore district, southern Poland: A combined pedological, geochemical and mineralogical approach. Applied Geochemistry 139, 105218. https://doi.org/10.1016/j.apgeochem.2022.105218
101. Thompson, R., Oldfield, F., 1986. Environmental Magnetism. Allen and Unwin, London. https://doi.org/10.1007/978-94-011-8036-8
102. Uzarowicz, Ł., Charzyński, P., Greinert, A., Hulisz, P., Kabała, C., Kusza, G., Kwasowski, W., Pędziwiatr, A., 2020a. Studies of technogenic soils in Poland: past, present, and future perspectives. Soil Science Annual 71(4), 281–299. https://doi.org/10.37501/soilsa/131615
103. Uzarowicz, Ł., Kwasowski, W., Lasota, J., Błońska, E., Górka-Kostrubiec, B., Tarnawczyk, M., Murach, D., Gilewska, M., Gryczan, W., Pawłowicz, E., Jankowski, P., 2025. Vegetation cover as an important factor affecting the properties and evolution of Spolic Technosols: A case study from a dump of the abandoned iron ore mine in central Poland. Catena 254, 108906. https://doi.org/10.1016/j.catena.2025.108906
104. Uzarowicz, Ł., Kwasowski, W., Śpiewak, O., Świtoniak, M., 2018a. Indicators of pedogenesis of Technosols developed in an ash settling pond at the Bełchatów thermal power station (central Poland). Soil Science Annual 69(1), 49–59. https://doi.org/10.2478/ssa-2018-0006
105. Uzarowicz, Ł., Skiba, S., 2011. Technogenic soils developed on mine spoils containing iron sulphides: Mineral transformations as an indicator of pedogenesis. Geoderma 163(1–2), 95–108. https://doi.org/10.1016/j.geoderma.2011.04.008
106. Uzarowicz, Ł., Skiba, M., Leue, M., Zagórski, Z., Gąsiński, A., Trzciński, J., 2018b. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part II. Mineral transformations and soil evolution. Catena 162, 255–269. https://doi.org/10.1016/j.catena.2017.11.005
107. Uzarowicz, Ł., Swęd, M., Kwasowski, W., Pędziwiatr, A., Kaczmarek, D., Koprowska, D., Górka-Kostrubiec, B., Pawłowicz, E., Murach, D., 2024. Initial pedogenic processes, mineral and chemical transformations and mobility of trace elements in Technosols on dumps of the former copper mines in Miedziana Góra and Miedzianka, the Świętokrzyskie Mts., south-central Poland. Catena 245, 108293. https://doi.org/10.1016/j.catena.2024.108293
108. Uzarowicz, Ł., Wolińska, A., Błońska, E., Szafranek-Nakonieczna, A., Kuźniar, A., Słodczyk, Z., Kwasowski, W., 2020b. Technogenic soils (Technosols) developed from mine spoils containing Fe sulphides: Microbiological activity as an indicator of soil development following land reclamation. Applied Soil Ecology 156, 103699. https://doi.org/10.1016/j.apsoil.2020.103699
109. Uzarowicz, Ł., Zagórski, Z., Mendak, E., Bartmiński, P., Szara, E., Kondras, M., Oktaba, L., Turek, A., Rogoziński, R., 2017. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. Properties, classification, and indicators of early pedogenesis. Catena 157C, 75–89. https://doi.org/10.1016/j.catena.2017.05.010

110. Van Oorschot, I.H.M., Dekkers, M.J., 1999. Dissolution behaviour of fine-grained magnetite and maghemite in the citrate-bicarbonate-dithionite extraction method. Earth and Planetary Science LetteFrs 167(3-4), 283–295.
111. Van Ranst, E., Wilson, M.A., Righi, D., 2018. Spodic Materials. [In:] Stoops, G., Marcelino, V., Mees, F. (Eds.), Interpretation of Micromorphological Features of Soils and Regoliths (Second Edition). Elsevier, pp. 633–662. https://doi.org/10.1016/B978-0-444-63522-8.00022-X
112. Van Reeuwijk, L.P., 2002. Procedures for soil analysis. Technical Paper 9. ISRIC, Wageningen.
113. Verrecchia, E.P., Trombino, L., 2021. A Visual Atlas for Soil Micromorphologists. Springer, Cham.
114. Walker, A., 1983. The effects of magnetite on oxalate- and dithionite-extractable iron. Soil Science Society of America Journal 47, 1022–1026.
115. Warchulski, R., Szczuka, M., Kupczak, K., 2020. Reconstruction of 16th–17th century lead smelting processes on the basis of slag properties: a case study from Sławków, Poland. Minerals 10(11), 1039. https://doi.org/10.3390/min10111039
116. Warzyński, H., Sosnowska, A., Harasimiuk, A., 2018. Effect of variable content of organic matter and carbonates on results of determination of granulometric composition by means of Casagrande's areometric method in modification by Prószyński. Soil Science Annual 69(1), 39–48. https://doi.org/10.2478/ssa-2018-0005
117. Wasak, K., 2014. Cellulose decomposition rate and features of organic matter in forest soils in the Tatra Mountains. Fundamental and Applied Soil Science 15, 70–80. https://doi.org/10.15421/041407
118. Wasak, K., Drewnik, M., 2015. Land use effects on soil organic carbon sequestration in calcareous Leptosols in former pastureland-a case study from the Tatra Mountains (Poland). Solid Earth 6, 1103–1115. https://doi.org/10.5194/se-6-1103-2015
119. Wasak, K., Drewnik, M., 2016. Properties of humus horizons of soils developed in the lower montane belt in the Tatra Mountains. Polish Journal of Soil Science 45, 57. https://doi.org/10.17951/PJSS.2012.45.1.57
120. Wasak-Sęk, K., 2017. Wpływ materiału macierzystego i roślinności na właściwości materii organicznej gleb regla dolnego w Tatrach Zachodnich. PhD Dissertation, Jagiellonian University in Kraków.
121. Watteau, F., Séré, G., Huot, H., Begin, J.C., Schwartz, C., Qiu, R., Morel, J.L., 2017. Micropedology of SUITMAs. [In:] Levin, M.J., Kim, K.-H.J., Morel, J.L., Burghardt, W., Charzyński, P., Shaw, R.K., IUSS Working Group SUITMA (Eds.), Soils within Cities, Global approaches to their sustainable management: Stuttgart, Germany, Catena Soil Sciences, Schweizerbart Science Publishers, pp. 84–92.
122. Watteau, F., Huot, H., Morel, J.-L., Rees, F., Schwartz, C., Séré, G., 2018. Micropedology to reveal pedogenetic processes in Technosols. Spanish Journal of Soil Science 8(2), 148–163. https://doi.org/10.3232/SJSS.2018.V8.N2.02
123. Watteau, F., Jangorzo, N. S., Schwartz, C., 2019. A micromorphological analysis for quantifying structure descriptors in a young constructed Technosol. Boletín de la Sociedad Geológica Mexicana 71(1), 11–20. https://doi.org/10.18268/bsgm2019v71n1a2
124. Watteau, F., Morel, J. L., Liu, C., Tang, Y., Huot, H., 2025. Technosol micromorphology reveals the early pedogenesis of abandoned rare earth element mining sites undergoing reclamation in south China. Minerals 15(5), 514. https://doi.org/10.3390/min15050514
125. Wieczorek, J., Zadrożny, P., 2013. Content of Cd, Pb and Zn in podzols Tatra National Park. Proceedings of ECOpole 7(1), 57. https://doi.org/10.2429/proc.2013.7(1)057
126. Woś, B., Tahsin Karimi Nezhad, M., Mustafa, A., Pietrzykowski, M., Frouz, J., 2023. Soil carbon storage in unreclaimed post mining sites estimated by a chronosequence approach and comparison with historical data. Catena 220A, 106664. https://doi.org/10.1016/j.catena.2022.106664

127. Zaiets, O., Poch, R.M., 2016. Micromorphology of organic matter and humus in Mediterranean mountain soils. Geoderma 272, 83–92. https://doi.org/10.1016/j.geoderma.2016.03.006
128. Zamanian, K., Pustovoytov, K., Kuzyakov, Y., 2016. Pedogenic carbonates: Forms and formation processes. Earth-Science Reviews 157, 1–17. https://doi.org/10.1016/j.earscirev.2016.03.003
129. Zanuzzi, A., Arocena, J.M., Van Mourik, J.M., Cano, A.F., 2009. Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology. Geoderma 154, 69–75. https://doi.org/10.1016/j.geoderma.2009.09.014
130. Zasoński, S., Niemyska-Łukaszuk, J., 1977. Soil types of Mt. Zgorzelisko based on chemical and micromorphological properties. Soil Science Annual 28(1), 243–261.
131. Zikeli, S., Jahn, R., Kastler, M., 2002. Initial soil development in lignite ash landfills and settling ponds in Saxony-Anhalt, Germany. Journal of Plant Nutrition and Soil Science 165(4), 530–536. https://doi.org/10.1002/1522-2624(200208)165:4%3C530::AID-JPLN530%3E3.0.CO;2-J
132. Zwoliński, S., 1984. Wpływ hut zakopiańskich na lasy tatrzańskie. Parki Narodowe i Rezerwaty Przyrody 5(1), 43–50.

Artykuły składające się na rozprawę doktorską

Artykuł 1: **Tarnawczyk M.**, Uzarowicz Ł., Kwasowski W., Górka-Kostrubiec B., Pędziwiatr A., 2025. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena 247, 108521. https://doi.org/10.1016/j.catena.2024.108521

(MNiSW: 140 pkt; IF: 5.7)

Arttkuł 2: **Tarnawczyk M.**, Uzarowicz Ł., Pędziwiatr A., Kwasowski W., 2025. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. Soil Science Annual 76(3), 211370. https://doi.org/10.37501/soilsa/211370

(MNiSW: 70 pkt; IF: 1.0)

Artykuł 3: **Tarnawczyk M.**, Uzarowicz Ł., Kwasowski W., Pędziwiatr A., Martín-Peinado F.J., 2025. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. Minerals 15(9), 988. https://doi.org/10.3390/min15090988

(MNiSW: 100 pkt; IF: 2.2)

Catena 247 (2024) 108521

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland

Magdalena Tarnawczyk [a,*], Łukasz Uzarowicz [a], Wojciech Kwasowski [a], Beata Górka-Kostrubiec [b], Artur Pędziwiatr [a]

[a] Warsaw University of Life Sciences – SGGW, Institute of Agriculture, Department of Soil Science, Nowoursynowska Str. 159, Building No. 37, 02-776 Warsaw, Poland
[b] Institute of Geophysics, Polish Academy of Sciences, Księcia Janusza Str. 64, 01-452 Warsaw, Poland

ARTICLE INFO

Keywords:
Technogenic soils
Alpine environment
Soil-forming factors
Soil genesis
Historical mining
Historical smelting

ABSTRACT

The Tatra Mountains are a unique Central European alpine ecosystem where the non-anthropogenic soil cover and soil-forming processes are well recognized. However, the Technosols in the area's high-mountain environment have not been studied in detail to date. Therefore the aim of this study was to identify the most important soil-forming factors controlling the properties of Technosols developed in historical mining and metallurgical sites in the Tatra Mountains of southern Poland active from the 15th Century until the end of the 19th. The present paper is one of the first attempts to study the genetic aspects of high-mountain Technosols in the temperate climatic zone. The study involved determining soil morphology and classification, soil properties, magnetic susceptibility, mineral composition, optical microscopic observations and total concentration of major elements. The studied Technosols were poorly developed soils with simple soil morphology (mainly A horizon in the topsoil and C horizons in the subsoil). There was a high content of rock fragments. The research has shown that the properties of Technosols in the Tatra Mountains were primarily determined by past human activities like mining and metallurgy as well as the type of anthropogenic parent material, which included mining wastes and metallurgical slags and determined soil properties together with mineral and chemical composition. Soil formation was significantly influenced by vegetation which was conditioned by the relief and climatic conditions dependent on altitudinal zonation. Vegetation and plant-derived soil organic matter shaped topsoil properties. The lengthy soil-forming process acting since a few centuries in some Technosols led to the formation of Bw horizons.

1. Introduction

The Tatra Mountains are a unique Central European alpine ecosystem. The majority are part of the Tatra National Park, which belongs to the UNESCO World Network of Biosphere Reserves. Currently, this is a protected area, but in the past it was the site of extensive mining and metallurgical processing. Industrial activity in the Tatra Mountains has a long history and can be divided into two periods. The first (from medieval times up to 18th Century) was mainly related to the extraction and smelting of non-ferrous metals (mainly copper and silver), while the second (in the 2nd half of the 18th Century and in 19th Century) involved the exploitation and smelting of iron and manganese ores (Jost, 1962; Paulo, 1979). Mining and metallurgical processing of metal ores in the Tatra Mountains ceased at the end of the 19th Century.

Ore mining and metal smelting leads to the creation of solid wastes commonly disposed of on the land surface. Mine wastes consist of rocks extracted from underground and not used for further processing, whereas metallurgical wastes are mainly slag produced by ore smelting accompanying by other smelter waste. The disposal sites are subject to plant colonization once the industrial areas are abandoned. Due to spontaneous plant succession, technogenic soils (Technosols) start to develop on the surface of mine heaps and metallurgical slag disposal sites. Technosols soils develop from industrial wastes of this kind. Their properties and pedogenesis are dominated by their technical origin (IUSS Working Group WRB, 2022). These soils contain a considerable concentration of artefacts, made or strongly altered by humans or

* Corresponding author.
E-mail address: magdalena_tarnawczyk@sggw.edu.pl (M. Tarnawczyk).

https://doi.org/10.1016/j.catena.2024.108521
Received 1 July 2024; Received in revised form 27 October 2024; Accepted 29 October 2024
Available online 4 November 2024

extracted from greater depths. Technogenic soils have recently been among the most intensively studied soil groups in different parts of the globe (Néel et al., 2003; Huot et al., 2015; Uzarowicz et al., 2020b) though high-mountain Technosols are poorly recognized. Technogenic soils commonly occur in industrial areas and are therefore often referred to as SUITMAs (Soils of Urban, Industrial, Traffic, Mining and Military Areas) and urban or mine soils (Lal and Stewart, 2017; Rate, 2022). A common feature of Technosols on heaps is their high heterogeneity. Their profile is generally poorly developed, although pedogenesis effects can be observed on old heaps (Huot et al., 2015; Ivanov et al., 2009; Uzarowicz and Skiba, 2011). Technogenic materials deposited on heaps can be a source of potentially toxic trace elements (Ciarkowska and Miechówka, 2022; Tarnawczyk et al., 2021; Uzarowicz et al., 2020a) and may pose a threat to the local environment, including soil, water and plants mainly due to the release of trace elements during the weathering of the technogenic soil substrate.

The literature about historical mining and smelting areas in the Tatra Mountains to date focuses mainly on the history of mining in the Tatra Mountains, the location and prospection of ores, the methods of their extraction and the analysis of available source materials (Dmytrowski and Kicińska-Świderska, 2006; Jach, 2002; Paulo and Panajew, 2006; Wątocki, 1950; Zwoliński, 1960). Moreover, the remnants of historical mining and smelting activity (drifts, shafts, mining heaps, steelworks and slags) in the Tatra Mountains are subject to geological studies (Hrouda and Kahan, 1991; Jach and Dudek, 2005; Sitarz et al., 2021). The current status of some of the adits of iron, manganese and polymetallic ores in the Chochołowska Valley and Kościeliska Valley areas were also inventoried, as well as basic mineralogical studies on collected samples (Pawlikowski et al., 2014).

Previous pedological studies in the Tatra Mountains are numerous and they involve, until now, the following native (non-anthropogenic) soil-related topics (1) effect of climate on the soil properties and the tendency to altitudinal soil zonality (Oleksynowa and Skiba, 1977; Skiba, 1983, 1985), (2) influence of geomorphological processes on soil cover (Drewnik, 2008), (3) soil geochemistry (Miechówka, 1989; Oleksynowa et al., 1977), (4) soil mineralogy with emphasis on clay minerals in soils (Skiba, 2007; Skiba et al., 2011), (5) properties of organic soils and forms of humus (Miechówka and Ciarkowska, 1998; Niemyska-Łukaszuk, 1977; Wasak and Drewnik, 2015, 2016; Stolarczyk et al., 2024), (6) biological activity of soil (Drewnik, 2006; Miechówka et al., 2021; Wasak, 2014), (7) concentration of heavy metals in soil (Miechówka and Niemyska-Łukaszuk, 2004; Wieczorek and Zadrożny, 2013; Ciarkowska and Miechówka, 2022), (8) concentration of radionuclides in soil (Kubica et al., 2002, 2007) and (9) soil classification (Komornicki and Skiba, 1996; Kubica et al., 2002; Skiba, 1983; Strzemski, 1956). However, soil studies on historical mining and smelting are very rare. The properties, mineral composition, origin and classification of Technosols in the Tatra Mountains have not been investigated in detail to date. Recently, a study was carried out to determine the factors controlling the concentration and spatial distribution of Zn, Pb and Cd in non-forest Tatra-Mountain soils (Ciarkowska and Miechówka, 2022). It was found that historical ore mining may contribute to metal concentration in soil in the Tatra Mountains. However, the studies by Ciarkowska and Miechówka (2022) did not focus on genesis and functioning of Tatra-Mountain Technosols.

The objective of this study was to determine the most important soil-forming factors controlling morphology, physico-chemical properties, mineral composition and major element content in Technosols developed in historical mining and metallurgical sites in the Tatra Mountains, southern Poland. To the best author's knowledge, the paper will be the first attempt to study the relationship between soil-forming factors and properties of high-mountain environment Technosols. We hypothesise that the development of Technosols in the high mountains is controlled by similar factors influencing genesis of native mountain soils (parent material, relief and morphogenetic processes, climatic conditions related with altitude, water, plant cover, human activity and time), of which past human activity (mining and smelting) and diversity of technogenic parent materials are expected to be the most important factors. The study extends the knowledge on the properties, origin and evolution of high-mountain Technosols in the temperate climatic zone with the Tatra Mountains as an example.

2. Materials and methods

2.1. Characterization of Tatra-Mountain environmental conditions

The research was conducted in the Tatra Mountains, southern Poland (Fig. 1). The Tatra Mountains are a unique alpine environment at an altitude reaching 2655 m a.s.l. (the Gerlach peak) with typical climatic-plant zonality. The lowest is the lower forest zone extending up to about 1250 m a.s.l. It consists mainly of beech (*Fagus silvatica* L.) and fir (*Abies alba* Mill.) though spruce (*Picea abies* (L.) H. Karst) is also common as it was introduced by human in past forest management practices. The upper forest zone, in which spruce and silver birch (*Betula pendula* Roth) predominate, extends from about 1250 m up to 1550 m a.s.l. Above that at 1550–1800 m a.s.l. there is the subalpine zone where dwarf pine (*Pinus mugo* Turra) shrubs make up the predominating plant community. The alpine meadow zone is at 1800–2300 m a.s.l., and is dominated by alpine grasslands including species like *Juncus trifidus* and *Festuca varia*. The subnival zone (above 2300 m a.s.l.) is the highest in the Tatra Mountains. It is characterized by harsh climatic conditions and a predominance of lichens, mosses and low grasses (Piękoś-Mirkowa and Mirek, 1996).

The Tatra Mountains have a subalpine and alpine climate, with high precipitation and low temperatures. Annual precipitation increases with altitude – from 1150 mm at the foot of the mountains up to around 1800 mm on Kasprowy Wierch (1987 m a.s.l.). The average annual temperature is 6 °C at the foothills and −4°C on the summits.

The mosaic pattern is very characteristic for the soil cover in the Tatra Mountains (Komornicki and Skiba, 1996). The soils reveal diverse properties and are formed from various igneous, sedimentary and metamorphic rocks (Komornicki and Skiba, 1996). Vegetation, which is dependent on vertical zonality and affects soil through organic matter input. Human activities like logging and tourism influence soil formation and fertility. Harsh climatic conditions affect the rate of soil formation and the type of vegetation present (Komornicki and Skiba, 1996; Nyka, 1969; Skrzydłowski 2013). Due to the alpine relief, steep slopes and intense rainfall, soil erosion is a common feature in the Tatra Mountains, which can affect the soil depth, structure and fertility, making it difficult for vegetation to grow (Fidelus-Orzechowska et al., 2021).

Podzols are typical Tatra-Mountain soils where non-carbonate rocks occur as soil parent materials (Komornicki and Skiba, 1996). Podzols commonly develop in coniferous forests. Rendzina soils (Rendzic Leptosols) develop on carbonate rocks. Brown soils (Cambisols) occupy relatively small areas in the lower alpine forests of the Tatra Mountains (Komornicki and Skiba, 1996; Ciarkowska and Miechówka, 2022) where they, together with rendzinas, provide habitats for different variants of beech and beech-fir forests. Above the tree line, initial soils like Leptosols and Regosols are common. There are also remnants of cryogenic soils which formed in the Tatra Mountains during past cold periods as an effect of cryogenic processes (Oleksynowa and Skiba, 1977).

2.2. Study area

Field studies were conducted in eight selected historical mining and smelting areas: (I) Huciańskie Banie (Mn and Fe ore mine), (II) mouth of the Kościeliska Valley (Fe ore mine), (III) Kościeliska Valley near the Ornak tourist shelter (Cu and Ag ore prospection adit), (IV) Pyszniańska Valley (Cu, Ag and Fe ore mine), (V) Żleb pod Banie (Pod Banie Couloir) at the Ornak ridge (Cu, Fe and Ag ore mine), (VI) Banisty Żleb (Banisty Couloir) at the Ornak ridge (Cu, Ag, Sb and Fe ore mine), (VII)

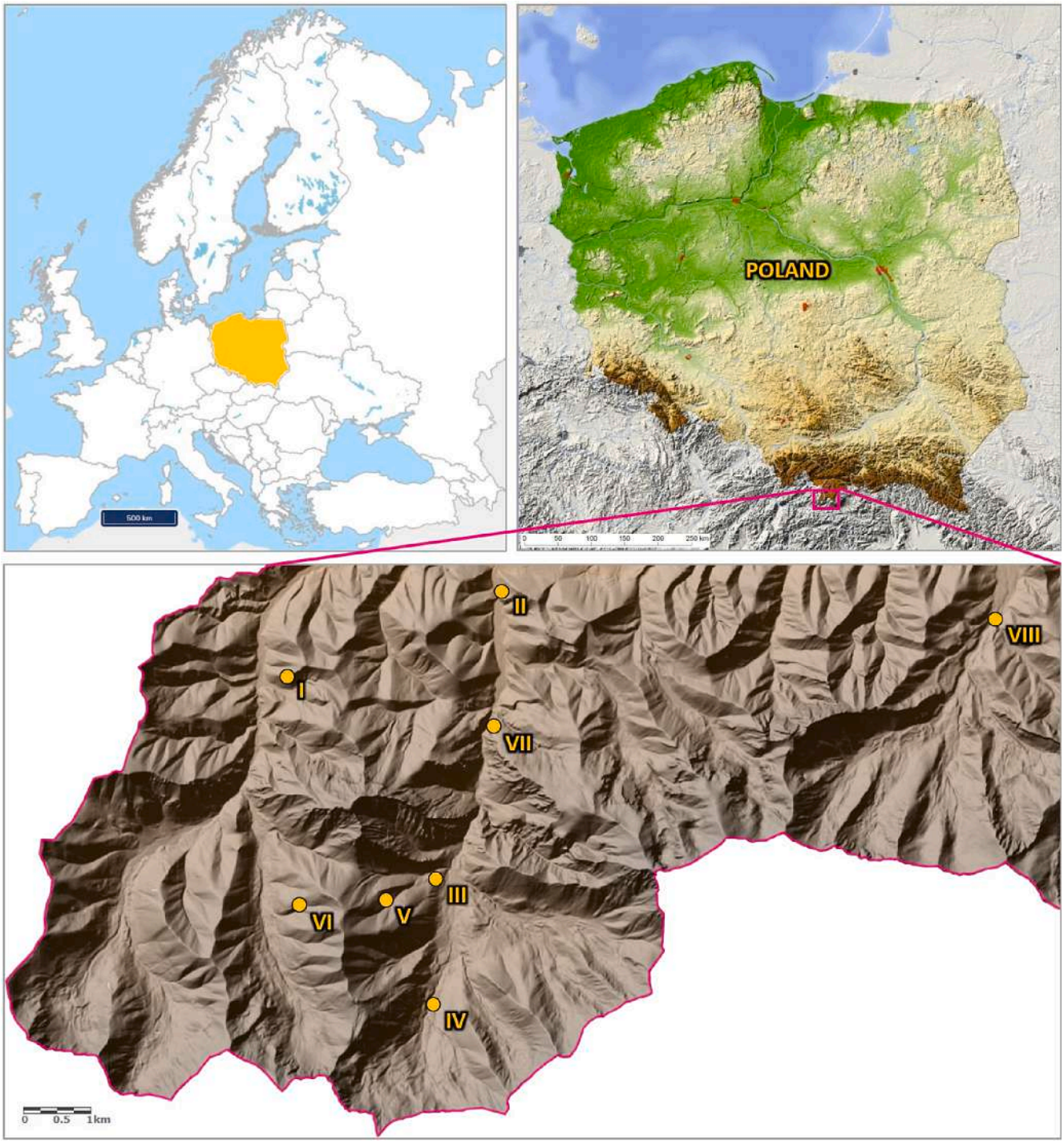


Fig. 1. Location of the study sites. I – Huciańskie Banie (Profile 1 and 2); II – Mouth of the Kościeliska Valley (Profile 3); III – Kościeliska Valley near the Ornak tourist shelter (Profile 4); IV – Pyszniańska Valley (Profile 5 and 6); V – Żleb pod Banie (Pod Banie Couloir) at the Ornak ridge (Profile 7 and 8); VI – Banisty Żleb (Banisty Couloir) at the Ornak ridge (Profile 9 and 10); VII – Kościeliska Valley – old steelwork at Stare Kościeliska (Profile 11 and 12); VIII – Kuźnice steelwork area (Profile 13). (sources: www.mapsforeurope.org; www.tablicaszkolna.pl; www.geoportal.gov.pl).

Kościeliska Valley – an old steelworks (a former iron and non-ferrous metal smelting area at Stare Kościeliska) and (VIII) the Kuźnice steelworks area (metal smelter) (Fig. 1).

At Huciańskie Banie site in the Chochołowska Valley, where Profiles 1 and 2 were located, manganese-bearing organodetritic limestones of the Lower Jurassic occur (Pawlikowski et al., 2014). Native copper has also been observed in these limestones (Górecki and Sermet, 2012). Hematite iron ore occurring in the red Jurassic limestones was also mined there. Profile 3 was located near an adit at the mouth of the Kościeliska Valley, at Kopka Kościeliska hill, where iron ores embedded in soft Triassic carbonate rocks were mined (Wątocki, 1950).

The oldest mining drifts in the Tatra Mountains were created in the Pyszniańska Valley (Profile 5 and 6) and on slopes of the Ornak ridge (Profile 4, 7, 8, 9 and 10) (Fig. 1). Copper and silver ore veins in granite and gneiss were exploited there (Wątocki, 1950). Particularly intensive mining works and prospecting for silver, copper and iron ores were carried out on the western slopes of Ornak at Banisty Żleb (Profile 9 and 10).

The largest centres of ore smelting (old steelworks) in the Tatra Mountains were located in the Kościeliska Valley at Stare Kościeliska (Profile 11 and 12) and in the Bystry Valley at Kuźnice (Profile 13) (Fig. 1). They processed metal ores extracted, among others, in the Kościeliska Valley (including Pyszniańska Valley) and on the Ornak ridge (Pawlikowski and Wróbel, 2013).

2.3. Study object

Thirteen soil profiles (P1–P13) were studied during the field works in July 2020 (Fig. 2). Soil profiles represented the most important and the best-preserved areas of historical mining and metallurgical activity in the Tatra Mountains reflecting the great variability of different types of mine and metallurgical wastes. In this study, we decided to consider one or two soil profiles representing one study site. The profiles were located on small heaps at the mouths of adits, in the vicinity of the old shaft and in the vicinity of the old steelworks. Field reconnaissance in each study site was completed prior to the preparation of each soil profile. The study sites varied in type of anthropogenic parent material like mining wastes and metallurgical slags, which differed in petrology and mineral composition of rock fragments occurring in soils as well as in soil properties. Moreover, different vegetation types were considered to assess the influence of plant cover on soil properties. Samples were taken from different topographic conditions, taking into account elevation, landforms and climatic conditions (Table 1). Also, the period of activity of mines and smelters was included to assess how the duration of soil-forming processes may influence soil properties and profile development.

Soil samples were taken from the soil horizons distinguished in soil profiles during field works. The analyses were carried out on a total of 56 soil samples (including 15 organic soil and 41 mineral soil samples). Soils were described in the field according to FAO guidelines (Jahn et al., 2006). The soil profiles were classified according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2022) and Polish Soil Classification (Kabała et al., 2019; Polish Soil Classification, 2019). Location, soil classification, geomorphological settings, and vegetation around studied soil profiles was presented in Table 1.

2.4. Laboratory analyses

2.4.1. Soil properties

Soil samples taken from each soil horizon were analysed in the laboratory. Living roots and organic residues were removed from soil samples, which were then dried at room temperature and sieved through a 2 mm sieve in order to obtain fine earth (<2 mm). The fine earth properties were determined by means of common pedological methods (Pansu and Gautheyrou, 2006; Soil Science Division Staff, 2017; Van Reeuwijk, 2002). Particle size distribution was measured by the Bouyoucos–Casagrande method modified by Prószyński (Warzyński et al., 2018). Soil textural classes were defined according to the USDA classification (Soil Science Division Staff, 2017). Soil pH was assessed using potentiometric method in H_2O using a soil/solution ratio of 1:2.5 (Pansu and Gautheyrou, 2006). Carbonate content was determined by means of the Scheibler volumetric method (reagent: 10 % w/w HCl) (Bąk, 1992). Total organic carbon (TOC), total nitrogen (TN) and total sulphur (TS) were determined using CHNS elemental analyser (the vario MACRO cube, Elementar) (Pansu and Gautheyrou, 2006). Inorganic (carbonate) C was subtracted in TOC calculations whenever a sample contained carbonates. The C/N ratio was calculated based on TOC and TN contents. Total phosphorous (TP) was determined on powdered soil fine earth by microwave sample mineralization (Milestone Ethos UP) in a mixture of concentrated acids (2 ml HNO_3 + 5 ml HF + 2 ml HCl + 1 ml $HClO_4$) and analysis of extracts using inductively coupled plasma – optical emission spectrometry (ICP-OES, Perkin Elmer, Avio 200).

Exchangeable acidity (EA) was measured by means of the Sokolov method (extraction using 1 mol·dm^{-3} potassium chloride and titration using 0.05 mol·dm^{-3} NaOH) (Brogowski and Czerwiński, 2016). Exchangeable bases (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) were extracted using ammonium acetate (pH = 7.0) and ammonium chloride (pH = 8.2) in non-carbonate and carbonate-bearing soil samples respectively (Ostrowska et al., 1991). Contents of exchangeable bases (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) in extracts were determined using ICP-OES method (Perkin Elmer, Avio 200). The sum of exchangeable bases (EB) was then calculated. Cation exchange capacity (CEC) was obtained as a sum of EA and EB. Base saturation (BS) was shown as a percentage of EB in CEC.

2.4.2. Soil magnetic susceptibility

The mass-specific magnetic susceptibility (χ) i.e., volume magnetic susceptibility (κ) normalized by a mass unit of the samples was measured using a multifunction MFK1-FA Kappabridge (AGICO, Brno, Czech Republic) at a frequency of 976 Hz with an intensity of 200 Am^{-1}. For each sample, the κ parameter was measured three times and the average value was calculated. The samples were weighed with an accuracy of ± 1 mg for the analyses. The χ parameter, which is commonly used in environmental studies, depends on the content of magnetic particles, their mineralogy and grain-size distribution (Thompson and Oldfield, 1986).

2.4.3. Soil mineral composition

Fine-earth (<2 mm) sample bulk mineral composition was determined using the powder X-ray diffraction method (XRD). The samples were powdered in an agate mortar prior to analyses. The Bruker AXS D5005 diffractometer equipped with the KRISTALLOFLEX® 760 X-ray generator, vertical goniometer, 1 mm divergence slit, 2 mm anti-scatter slit and 0.6 detector slit and a graphite diffracted-beam monochromator was used. CoKα radiation was applied with the voltage of 40 kV and 30 mA current. Random mounts of the ground materials were scanned from 3 to 70 °2θ at a counting time of 1 s per 0.02° step on a rotating stage. XRD analyses were performed in the Department of Soil Science, Warsaw University of Life Sciences – SGGW (WULS–SGGW), Poland. Mineral symbols were used in accordance with international standards (Warr, 2021).

2.4.4. Optical microscopy observations

Undisturbed soils blocks were taken from selected soil horizons. They were air-dried and embedded with Araldite 2020 epoxy resin. Polished thin sections were prepared from the impregnated soil blocks and examined in transmitted light under petrographic microscopes (Olympus SZX Z10 and Olympus BX41). Polished thin sections were prepared at the Faculty of Geology, University of Warsaw, Poland.

2.4.5. Total concentrations of major elements

In order to determine the contents of major elements, the soil samples were ground and mixed with $LiBO_2/Li_2B_4O_7$ flux. Crucibles were fused in a furnace. The cooled beads were dissolved in the American Chemical Society (ACS) grade nitric acid. Contents of major elements were analysed by ICP-AES method. Loss on ignition (LOI) was determined by igniting a sample split in 1000 °C, then measuring the weight loss. Analyses were carried out in the Bureau Veritas Minerals Laboratories (BVML), Canada.

2.5. Statistical analysis

Principal Component and Classification Analysis (PCCA) was used to identify the factors determining the properties of studied soils and distinguish soil groups with similar properties. The data was standardized prior to statistical analysis and the following properties were taken into account: magnetic susceptibility (χ), pH_{H2O}, content of carbonates ($CaCO_3$ eq.), EA, EB, BS as well as concentration of SiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, K_2O, and MnO. The number of principal components was selected based on the eigenvalues. The analysis was conducted in STATISTICA 13 (StatSoft).

Fig. 2. Studied soil profiles and their surroundings. P1, P2 – Huciańskie Banie (Mn and Fe ore mine); P3 – Mouth of the Kościeliska Valley (Fe ore mine); P4 – Kościeliska Valley near the Ornak tourist shelter (Cu and Ag ore prospection adit); P5, P6 – Pyszniańska Valley (Cu, Ag and Fe ore mine); P7, P8 – Żleb pod Banie (Pod Banie Couloir) at the Ornak ridge (Cu, Fe and Ag ore mine); P9, P10 – Banisty Żleb (Banisty Couloir) at the Ornak ridge (Cu, Ag, Sb and Fe ore mine); P11, P12 – Kościeliska Valley – old steelwork at Stare Kościeliska (the area of the former center of iron and non-ferrous metals smelting); P13 – Kuźnice steelwork area (metal smelter).

Table 1
Location, soil classification, geomorphological settings and vegetation around studied soil profiles.

Location and time of activity of the mining/smelting area	Soil profile	Soil classification	Geographical position (GPS)	Altitude (m a.s.l.)	Geomorphological settings	Vegetation
I. Huciańskie Banie (late 18th c. – mid-19th c.)	P1	WRB2022*: Spolic Technosol (Loamic, Eutric, Calcaric, Humic, Hyperartefactic, Skeletic, Toxic) PSC2019**: Industriosol (toxic)	49°15′38.3″ N 19°49 ′18.3″ E	1156	Slope 40 %, exposure NE	Meadow *(Poaceae, Ranunculus repens, Trifolium pratense, Taraxacum officinale, Geranium robertianum, Fragaria* sp., *Veronica* sp., *Polypodiopsida* sp., *Urtica dioica, Valeriana* sp.*)*, regenerating spruce forest
	P2	WRB2022*: Spolic Technosol (Loamic, Eutric, Calcaric, Humic, Hyperartefactic, Skeletic, Toxic) PSC2019**: Industriosol (toxic)	49°15′38.2″ N 19°49′18.1″ E	1155	Slope 40 %, exposure NE	
II. Mouth of the Kościeliska Valley (late 18th c. – 19th c.)	P3	WRB2022*: Spolic Technosol (Epiarenic, Endoloamic, Eutric, Dolomitic, Mollic, Hyperartefactic, Skeletic) PSC2019**: Industriosol	49°16′27.0″ N 19°52′8.5″ E	944	Slope 40 %, exposure W	Spruce forest (*Picea abies, Bromus* sp., *Bryophyta* sp., *Galium* sp., *Arctium* sp., *Cirsium* sp., *Fragaria* sp., *Hieracium* sp., *Orchis* sp., *Ranunculus* sp., *Daphne mezereum)*
III. Kościeliska Valley near the Ornak tourist shelter (late 18th c. – early 19th c.)	P4	WRB2022*: Spolic Technosol (Epiarenic, Endoloamic, Eutric, Humic, Hyperartefactic) PSC2019**: Industriosol	49°13′45.1″ N 19°51′16.4″ E	1112	Flat area on a dump	Spruce forest *(Picea abies, Sorbus* sp., *Rubus* sp., *Polypodiopsida* sp., *Urtica dioica, Myosotis* sp., *Bryophyta* sp.*)*
IV. Pyszniańska Valley (15th c. – late 19th c.)	P5	WRB2022*: Spolic Technosol (Arenic, Epidystric, Endoeutric, Protocambic, Humic, Hyperartefactic, Skeletic, Toxic) PSC2019**: Industriosol (toxic)	49°12′54.0″ N 19°51′21.7″ E	1189	Slope 30 %, exposure NE	Spruce forest (*Picea abies, Bryophyta* sp., *Vaccinium myrtillus, Polypodiopsida* sp., *Chamerion angustifolium, Rubus* sp., *Oxalis acetosella)*
	P6	WRB2022*: Spolic Technosol (Epiloamic, Endoarenic, Dystric, Protocambic, Humic, Hyperartefactic, Skeletic, Toxic) PSC2019**: Industriosol (toxic)	49°12′58.7″ N 19°51′22.2″ E	1189	Slope 45 %, exposure NW	
V. Żleb pod Banie (Pod Banie Couloir) at the Ornak ridge (15th c. – late 19th c.)	P7	WRB2022*: Spolic Technosol (Epiarenic, Endoloamic, Dystric, Humic, Hyperartefactic, Skeletic) PSC2019**: Industriosol (toxic)	49°13′36.7″ N 19°50′32.9″ E	1376	Slope 45 %, exposure E	Spruce forest (*Picea abies; Sorbus* sp., *Bryophyta* sp., *Vaccinium myrtillus, Polypodiopsida* sp.*)*
	P8	WRB2022*: Spolic Technosol (Arenic, Dystric, Humic, Hyperartefactic, Skeletic, Toxic) PSC2019**: Industriosol (toxic)	49°13′36.6″ N 19°50′33.6″ E	1373	Slope 45 %, exposure E	
VI. Banisty Żleb (Banisty Couloir) at the Ornak ridge (16th c. – 19th c.)	P9	WRB2022*: Coarsic Spolic Technosol (Arenic, Amphiloamic, Dystric, Ochric, Hyperartefactic, Skeletic, Toxic) PSC2019**: Industriosol	49°13′34.0″ N 19°49′44.2″ E	1590	Slope 30 %, exposure NW	*Pinus mugo* shrubs *(Vaccinium myrtillus, Bryophyta* sp., *Carex* sp., *Juncus trifidus, Calluna vulgaris, Rubus* sp.*)*
	P10	WRB2022*: Coarsic Spolic Technosol (Loamic, Dystric, Humic, Hyperartefactic, Skeletic, Toxic) PSC2019**: Industriosol (toxic)	49°13′34.7″ N 19°49′42.7″ E	1588	Slope 45 %, exposure NW	
VII. Kościeliska Valley – old steelwork at Stare Kościeliska (18th c. – early 19th c.)	P11	WRB2022*: Spolic Technosol (Epiarenic, Endoloamic, Eutric, Carbonic, Humic, Hyperartefactic, Pyric, Toxic)PSC2019**: Industriosol (toxic)	49°15′27.5″ N 19°52′5.9″ E	969	Flat area	Meadow (*Dactylis glomerata, Alchemilla* sp., *Ranunculus acris, Equisetum arvense, Myosotis* sp., *Urtica dioica, Trifolium pratense, Geum rivale, Rumex acetosa, Geranium phaeum, Campanula* sp., *Achillea millefolium, Cirsium* sp., *Galium* sp.*)*
	P12	WRB2022*: Spolic Technosol (Epiarenic, Endoloamic, Eutric, Carbonic, Humic, Hyperartefactic, Pyric, Toxic) PSC2019**: Industriosol (toxic)	49°15′27.5″ N 19°52′5.9″ E	969	Flat area	
VIII. Kuźnice steelworks (late 18th c. – late 19th c.)	P13	WRB2022*: Spolic Technosol (Arenic, Eutric, Humic, Hyperartefactic, Relocatic, Skeletic) PSC2019**: Industriosol	49°16′12.5″ N 19°58′51.2″ E	918	Slope 5 %, exposure N	Grasses and perenials (*Dactylis glomerata, Alchemilla* sp., *Potentilla anserina, Galium* sp., *Urtica dioica, Trifolium repens)*

3. Results

3.1. Soil morphology and classification

The studied Technosol profiles were weakly developed soils. All profiles had simple soil morphology with O and A (AC) horizons in the topsoil and C horizons (diverse anthropogenic parent materials) in the subsoil (Fig. 2). The exception were Profiles 5 and 6 in which weakly developed Bw horizons occurred. There was a high rock-fragment content in the majority of the examined soil profiles (Table 2).

Technosols developed from mining wastes were represented by ten profiles (Profiles 1–10) (Fig. 2). Profiles 1 and 2 at Huciańskie Banie in the Chochołowska Valley were located on a small heap near the adit of an old Fe and Mn ore mine. Soil material contained numerous sedimentary rock fragments (grey limestones) surrounded by loamy material with grey and red colours (Table 2). Profile 3 at the mouth of the Kościeliska Valley was developed at close vicinity of an adit of the abandoned Fe ore mine. The substrate consisted of dolomite debris surrounded by a loamy soil substrate containing a high admixture of humus. Profile 4 occurred at a small heap in a higher part of the Kościeliska Valley where copper and silver ores were prospected. It had a clearly visible A horizon in the topsoil and brown soil substrate in the subsoil (Fig. 2). Profiles 5 and 6 were developed on heaps near the collapsed shafts in the Pyszniańska Valley where copper, silver and iron ores were exploited. The soils are rich in granite and gneiss fragments. Thick O horizons (up to 10 cm) were distinguished in the topsoil. Brownish horizons were found in the central part of profiles. These horizons were labelled as Bw horizons which suggest the possible effect of some more advanced soil-forming processes (brownification or podzolization). Profiles 7 and 8 were developed on small heaps near old copper mines in Żleb pod Banie (Pod Banie Couloir) at the eastern slopes of the Ornak ridge covered with spruce forest. Profiles 9 and 10 were developed on a mine waste debris deposited near an old copper mine in Banisty Żleb (Banisty Couloir) at the western slopes of the Ornak ridge covered with *Pinus mugo* shrubs. Profiles 7 and 8 had better-developed O and AC horizons than Profiles 9 and 10.

Technosols developed in the areas of old metallurgical activity were represented by three profiles (Profiles 11–13) (Fig. 2). Profiles 11 and 12 were located near the old steelworks at Stare Kościeliska in the Kościeliska Valley. These soils contained numerous slag fragments, ferruginous rocks, charcoals and building waste (e.g., brick fragments). Secondary Cu-bearing minerals (azurite, malachite) commonly covered slag fragments. Profile 12 was clearly layered. Profile 13 was located in Kuźnice where old steelworks were active in 19th Century. The profile was located in an artificial slag disposal site prepared in the vicinity of Tatra National Park headquarter about 10 years before the field works. The disposal site was constructed from carbonate-bearing sandy material covered with a layer of slag fragments brought in from the vicinity of the old steelworks in Kuźnice area. The effect was a thin bipartite Profile 13 (Fig. 2).

The studied soils were classified as different variants of Spolic Technosols characterized by various supplementary qualifiers (Hyperartefactic, Humic, Loamic, Skeletic, Toxic, Eutric, Epiarenic, Endoloamic, Dystric, Arenic, Calcaric, Protocambic, Carbonic, Pyric, Dolomitic, Mollic, Relocatic), and Coarsic Spolic Technosols with different supplementary qualifiers (Arenic, Amphiloamic, Dystric, Ochric, Hyperartefactic, Skeletic, Toxic, Loamic, Humic) (IUSS Working Group WRB, 2022) (Table 1), as well as Industriosols (toxic) (Kabała et al., 2019; Polish Soil Classification, 2019).

3.2. Physical and chemical soil properties

All investigated soils were characterized by a high contribution of rock fragments (majority of soil horizons were composed of > 50 % rock fragments, however numerous soil horizons contained up to 90 % rock fragments). The analysed soil fine-earth texture (< 2 mm) was mainly sandy loam and loamy sand (Table 2).

The pH_{H2O} of the studied soils was very diverse (from 3.6 to 8.6) (Table 2). High pH_{H2O} (up to 8.1) was typical of Profile 1, 2 and 3 in which carbonate rock fragments occurred in soil substrate. These soils contained high contents of carbonates (from 9.6 to 31.2 %). High pH_{H2O} was also a feature of Profile 13 subsoil where content of carbonates reached a value of 5.8 %. High pH_{H2O}, despite the lack of carbonates, was typical of Profile 4, 11 and 12. In profile 12, carbonates occurred only in 3C horizon (1.7 % of carbonates). The lowest pH_{H2O} (from 3.6 to 6.0) was characteristic feature of Profiles 5–10 (Table 2) developed from non-carbonate mine wastes containing fragments of granites and gneisses. Regardless of soil parent material, soil pH_{H2O} within all studied soil profiles was typically the lowest in the topsoil where soil organic matter (SOM) was accumulated. The highest acidity occurred in the topsoil of Technosols covered with coniferous vegetation (Table 1) like Profiles 5–10 located in the Pyszniańska Valley, Żleb pod Banie and Banisty Żleb.

TOC contents were typically the highest in organic (O) horizons (up to 47.9 %) (Table 2). In the mineral horizons, TOC concentration was lower (from 0.29 to 14.69 %) and generally decreased with profile depth. The exception to this trend were profiles located near the old steelworks in the Kościeliska Valley. In the subsoil (C horizons) of Profile 11, TOC content increased with depth; however, in Profile 12, TOC was the highest (14.69 %) at the depth of 28–50 cm (2C horizon). Numerous fragments of anthropogenic charcoals were found in Profiles 11 and 12. In the soil mineral horizons in post-mining areas (Profile 1–10), TOC content average was 2.75 %, whereas it was 6.32 % on average in soils of the post-smelter areas (Profiles 11–13).

The highest TN contents were recorded in the organic horizons (from 0.9 to 2.06 %), whereas mineral horizons contained from 0.06 to 0.65 % of TN (Table 2). In the mineral horizons, the TN contents tended to decrease with soil depth. The C/N ratio ranged from 19 to 53 (31 on average) in organic horizons and from 5 to 94 in mineral horizons (22). The highest C/N ratio value was determined in 2C horizon of Profile 12 where numerous fragments of anthropogenic charcoals occurred.

TS content generally decreased with depth in the profiles. The highest contents were recorded in Profile 12 in the 3C horizon (0.75 %), in Profile 7 in the mineral horizons (0.37–0.53 %), and in Profile 10 in AC horizon (0.57 %) (Table 2). In the other horizons, TS content ranged from 0.01 to 0.16 %.

TP content ranged from 0.07 to 0.16 % in the organic horizons whereas, in the mineral horizons, it ranged from 0.05 to 0.76 % (Table 2). The highest contents were recorded in Huciańskie Banie (0.76 % in AC2 horizon of Profile 2) and in the old steelworks in the Kościeliska Valley (0.59 % in 2C horizon of Profile 12) though TP in the remaining soils ranged from 0.05 to 0.16 % throughout the profiles.

3.3. Sorption properties

Exchangeable acidity (EA) ranged from 0.04 to 18.58 cmol(+)·kg^{-1} in mineral horizons and from 2.78 to 15.26 cmol(+)·kg^{-1} in the Oe and Oa horizons (Table 3). The lowest EA were noted in Profiles 1, 2 and 3 in which soil material was slightly alkaline. High EA was the feature of the most acidic soils. The highest EA was recorded in AC horizon of Profile 7 located in Żleb pod Banie. In Profiles 11–13 containing metallurgical slags developed in the areas of old smelting activity, EA was averagely very low (0.09 cmol (+)·kg^{-1}) (Table 3).

The highest EB values were typical of Profile 1, 2 and 3 developed from mine wastes containing carbonate rocks (Table 3). The highest amounts of EB were found in Oe horizon of Profile 3. However, the lowest EB contents were noted in non-carbonate Profiles 4–10.

The CEC of the investigated soils averaged 22.7 cmol(+)·kg^{-1} (Table 3). Profiles 1, 2 and 3 had the highest CEC, whereas the non-carbonate soils had the lowest (Table 3). The CEC of the soils containing metallurgical wastes (e.g., slags) varied widely among profiles, which was associated with soil material heterogeneity. For example, 3C

Table 2
Selected physical and chemical properties of the studied soils.

Soil profile	Horizon	Depth (cm)	Munsell colour (moist)*	Rock fragments (%)*	Percentage of fractions (mm)			Soil textural class (USDA)	Magnetic susceptibility (χ) ($\times 10^{-8} \cdot m^3 \cdot kg^{-1}$)	pH_{H2O}	eq. $CaCO_3$ (%)	TOC (%)	TN (%)	C/N	TS (%)	TP (%)
					2.0–0.05	0.05–0.002	<0.002									
P1	Oi	0–1	–	–	–	–	–	–	–	–	–	42.40	1.46	29	0.10	–
	AC1	1–5	10YR 2/2	15	76	17	7	SL	83.5	7.4	20.5	8.19	0.56	19	0.08	0.33
	AC2	5–15	10YR 3/1	60	76	15	9	SL	91.4	7.9	31.2	2.18	0.12	48	0.04	0.29
	C	15–35	10YR 3/2	70	75	15	10	SL	36.8	8.0	30.4	1.85	0.07	76	0.04	0.31
	2C	35–60	2.5YR 3/3	80	54	30	16	SL	12.5	8.1	21.5	1.06	0.11	34	0.02	0.14
P2	Oi	0–1	–	–	–	–	–	–	–	–	–	43.97	0.98	45	0.07	–
	AC1	1–25	10YR 2/2	40	75	19	6	SL	32.2	7.5	22.1	6.62	0.44	21	0.06	0.60
	AC2	25–45	10YR 3/1	60	70	21	9	SL	33.7	7.9	21.2	2.63	0.17	31	0.03	0.76
	AC3	45–65	10YR 3/2	70	65	23	12	SL	32.6	7.9	20.8	2.42	0.15	32	0.04	0.66
	2C	65–90	2.5YR 3/2	80	46	40	14	L	22.4	7.8	9.6	2.70	0.24	16	0.04	0.19
P3	Oe	0–6	7.5YR 3/3	–	–	–	–	–	–	5.7	–	41.22	1.65	25	0.13	0.09
	O/C	6–25	10YR 2/1	70	87	9	4	LS	32.3	6.8	11.1	23.57	1.11	22	0.12	0.07
	AC	25–40	10YR 2/2	70	81	15	4	LS	15.1	7.2	17.0	10.69	0.53	24	0.07	0.07
	BC	40–60	10YR 3/4	40	70	24	6	SL	6.5	7.6	26.5	5.14	0.26	32	0.04	0.08
P4	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–13	10YR 2/2	50	85	11	4	LS	22.3	6.1	n	8.41	0.54	16	0.06	0.08
	C1	13–35	7.5YR 5/4	30	58	25	17	SL	8.0	6.8	n	0.49	0.07	7	0.02	0.05
	C2	35–60	10YR 5/4	30	57	25	18	SL	7.9	6.9	n	0.29	0.06	5	0.01	0.06
P5	Oe	0–3	10YR 2/2	–	–	–	–	–	–	4.1	–	44.95	2.06	22	0.15	0.16
	Oa	3–10	10YR 2/1	–	–	–	–	–	–	3.7	–	23.09	1.20	19	0.12	0.12
	A	10–15	10YR 2/1	50	86	11	3	LS	15.6	4.0	n	4.62	0.29	16	0.10	0.08
	Bw	15–20	10YR 3/3	70	78	18	4	LS	13.4	4.4	n	1.79	0.14	13	0.09	0.09
	C	20–45	10YR 4/2	90	77	19	4	LS	14.0	6.0	n	1.01	0.09	12	0.08	0.08
P6	Oe	0–2	10YR 2/2	–	0	0	0	–	–	4.0	–	37.86	1.67	23	0.14	0.13
	Oa	2–10	10YR 2/1	–	0	0	0	–	–	3.6	–	27.23	1.23	22	0.11	0.12
	ABw	10–20	10YR 3/3, 4/3	50	76	16	8	SL	10.2	3.9	n	1.16	0.10	12	0.06	0.09
	C	20–65	5YR 5/1	90	79	14	7	LS	10.8	5.5	n	0.63	0.07	9	0.16	0.10
P7	Oe	0–2	–	–	–	–	–	–	–	3.7	–	40.47	1.54	26	0.13	0.13
	AC	2–15	10YR 2/1	50	86	13	1	S	32.5	3.8	n	10.93	0.65	17	0.08	0.10
	C	15–50	10YR 3/4	70	65	32	3	SL	15.3	4.6	n	1.96	0.15	13	0.02	0.08
P8	Oe	0–4	–	–	–	–	–	–	–	4.0	–	46.96	1.58	30	0.12	0.15
	AC	4–15	10YR 2/2	40	81	18	1	LS	15.5	3.8	n	3.02	0.16	18	0.57	0.06
	C1	15–35	10YR 2/2	70	81	16	3	LS	11.8	4.5	n	1.26	0.10	13	0.15	0.06
	C2	35–55	10YR 3/4	80	79	18	3	LS	10.5	4.3	n	1.44	0.11	13	0.12	0.06
P9	Oi	0–2	–	–	–	–	–	–	–	–	–	45.82	0.91	50	0.08	–
	AC	2–10	10YR 3/2	80	79	15	6	LS	14.4	4.4	n	1.05	0.10	11	0.40	0.08
	C1	10–40	10YR 4/2	90	76	16	8	SL	14.4	4.5	n	0.88	0.09	10	0.37	0.09
	C2	40–80	10YR 4/2	90	79	15	6	LS	13.3	4.5	n	0.86	0.09	10	0.53	0.08
P10	Oi	0–1	–	–	–	–	–	–	–	–	–	47.90	0.90	53	0.07	–
	AC	1–10	10YR 3/2	70	76	17	7	SL	39.0	4.4	n	1.48	0.10	15	0.07	0.08
	C1	10–50	10YR 4/2	90	77	16	7	SL	14.8	4.4	n	1.16	0.09	12	0.07	0.09
	C2	50–70	10YR 4/4	70	76	18	6	SL	15.2	4.5	n	1.42	0.12	12	0.06	0.10
P11	Oi	0–1	–	–	–	–	–	–	–	–	–	40.20	1.22	33	0.09	–
	A	1–15	10YR 2/1	5	79	14	7	LS	3313.6	5.6	n	9.13	0.55	17	0.06	0.28
	C1	15–30	10YR 2/2, 4/3	10	65	26	9	SL	3342.2	6.0	n	5.24	0.29	18	0.04	0.27
	C2	30–45	10YR 2/1	15	67	27	6	SL	7064.4	6.2	n	8.84	0.28	32	0.04	0.45
	C3	45–60	10YR 2/1	20	69	26	5	SL	10485.6	6.5	n	10.60	0.22	47	0.04	0.53
P12	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–20	10YR 2/1	20	76	19	5	LS	4683.8	5.8	n	8.04	0.42	19	0.05	0.27
	C1	20–28	10YR 5/4	20	67	24	9	SL	489.4	6.1	n	2.55	0.21	12	0.10	0.12
	2C	28–50	10YR 2/1	50	65	29	6	SL	9480.3	6.1	n	14.69	0.16	94	0.03	0.59
	3C	50–60	5YR 4/4	40	70	23	7	SL	161.2	6.6	1.7	1.44	0.08	20	0.75	0.30
	4C	60–75	10YR 4/3	30	61	29	10	SL	36.6	6.4	n	1.87	0.18	10	0.05	0.10
P13	Oi	0–1	–	–	–	–	–	–	–	–	–	45.07	1.18	38	0.07	0.00
	AC	1–15	10YR 2/1	80	80	18	2	LS	128.0	7.0	1.3	6.03	0.38	16	0.10	0.10
	2C	15–25	10YR 5/3	50	84	11	5	LS	28.3	8.6	5.8	5.63	0.38	17	0.10	0.05

Explanations: – not analysed; n – not detected; * measured during field works; L – loam; LS – loamy sand; S – sand; SL – sandy loam; TOC – total organic carbon; TN – total nitrogen; TS – total sulphur; TP – total phosphorous.

Table 3
Sorption properties of the studied soils.

Soil profile	Horizon	Depth (cm)	EA	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	EB	CEC (EA + EB)	BS
			cmol(+)•kg^{-1}							(%)
P1	Oi	0–1	–	–	–	–	–	–	–	–
	AC1	1–5	0.12	43.46	1.23	0.45	0.00	45.2	45.3	99.7
	AC2	5–15	0.07	29.35	0.54	0.25	0.02	30.2	30.2	99.8
	C	15–35	0.07	23.92	0.44	0.06	0.02	24.5	24.5	99.7
	2C	35–60	0.07	21.76	0.68	0.10	0.01	22.6	22.6	99.7
P2	Oi	0–1	–	–	–	–	–	–	–	–
	AC1	1–25	0.07	35.12	0.55	0.29	0.00	36.0	36.0	99.8
	AC2	25–45	0.10	32.82	0.42	0.30	0.04	33.6	33.7	99.7
	AC3	45–65	0.09	32.49	0.42	0.27	0.02	33.2	33.3	99.7
	2C	65–90	0.09	29.47	0.39	0.15	0.03	30.0	30.1	99.7
P3	Oe	0–6	2.78	68.59	23.40	2.66	0.11	94.8	97.6	97.2
	O/C	6–25	0.22	52.54	18.02	0.29	0.09	70.9	71.2	99.7
	AC	25–40	0.12	37.07	9.66	0.12	0.10	47.0	47.1	99.7
	BC	40–60	0.13	21.61	5.60	0.06	0.02	27.3	27.4	99.5
P4	Oi	0–1	–	–	–	–	–	–	–	–
	A	1–13	0.09	18.80	8.80	0.21	0.03	27.8	27.9	99.7
	C1	13–35	0.04	5.48	3.18	0.12	0.02	8.8	8.8	99.6
	C2	35–60	0.04	4.38	2.80	0.14	0.02	7.4	7.4	99.4
P5	Oe	0–3	6.52	25.81	6.16	2.19	0.16	34.3	40.8	84.0
	Oa	3–10	13.13	10.24	1.79	0.79	0.10	12.9	26.1	49.6
	A	10–15	7.54	2.54	0.57	0.11	0.05	3.3	10.8	30.2
	Bw	15–20	4.81	1.71	0.76	0.08	0.00	2.6	7.4	34.7
	C	20–45	0.07	4.91	1.92	0.10	0.02	6.9	7.0	99.0
P6	Oe	0–2	6.64	17.31	3.06	1.54	0.15	22.1	28.7	76.9
	Oa	2–10	13.33	11.31	2.04	0.77	0.09	14.2	27.5	51.6
	ABw	10–20	9.98	0.45	0.28	0.11	0.02	0.9	10.8	7.9
	C	20–65	0.13	2.63	1.50	0.16	0.02	4.3	4.4	97.1
P7	Oe	0–2	15.26	5.49	3.61	2.63	0.18	11.9	27.2	43.8
	AC	2–15	18.58	0.53	0.74	0.35	0.07	1.7	20.3	8.3
	C	15–50	4.94	0.13	0.07	0.09	0.02	0.3	5.3	6.0
P8	Oe	0–4	8.49	8.30	3.94	3.93	0.15	16.3	24.8	65.8
	AC	4–15	4.36	0.25	0.31	0.17	0.02	0.7	5.1	14.5
	C1	15–35	1.79	0.35	0.43	0.12	0.02	0.9	2.7	34.0
	C2	35–55	2.45	0.20	0.26	0.11	0.03	0.6	3.1	19.8
P9	Oi	0–2	–	–	–	–	–	–	–	–
	AC	2–10	3.39	0.14	0.07	0.10	0.02	0.3	3.7	8.8
	C1	10–40	2.77	0.12	0.05	0.10	0.03	0.3	3.1	9.5
	C2	40–80	2.61	0.12	0.04	0.09	0.02	0.3	2.9	8.6
P10	Oi	0–1	–	–	–	–	–	–	–	–
	AC	1–10	3.76	0.13	0.05	0.08	0.00	0.3	4.0	6.3
	C1	10–50	3.21	0.08	0.02	0.06	0.01	0.2	3.4	5.0
	C2	50–70	3.46	0.06	0.02	0.06	0.02	0.2	3.6	4.7
P11	Oi	0–1	–	–	–	–	–	–	–	–
	A	1–15	0.12	27.68	3.47	0.42	0.02	31.6	31.7	99.6
	C1	15–30	0.30	23.91	1.82	0.13	0.04	25.9	26.2	98.8
	C2	30–45	0.06	33.65	1.29	0.08	0.09	35.1	35.2	99.8
	C3	45–60	0.07	43.69	1.13	0.08	0.07	45.0	45.0	99.9
P12	Oi	0–1	–	–	–	–	–	–	–	–
	A	1–20	0.08	23.64	2.38	0.11	0.05	26.2	26.3	99.7
	C1	20–28	0.07	10.63	0.84	0.08	0.02	11.6	11.6	99.4
	2C	28–50	0.05	50.57	2.16	0.12	0.07	52.9	53.0	99.9
	3C	50–60	0.05	0.49	0.37	0.02	0.04	0.9	1.0	94.6
	4C	60–75	0.05	10.56	1.12	0.09	0.03	11.8	11.9	99.6
P13	Oi	0–1	–	–	–	–	–	–	–	–
	AC	1–15	0.14	16.92	3.15	0.52	0.10	20.7	20.8	99.3
	2C	15–25	0.04	11.54	0.36	0.02	0.01	11.9	12.0	99.7

Explanations: – not analysed; EA – exchangeable acidity, EB – sum of exchangeable bases; CEC – cation exchange capacity; BS – base saturation of the sorption complex.

horizon of Profile 12 (Kościeliska Valley – old steelwork) had very low CEC compared to the other horizons in that profile where the average was 30.1 cmol (+)·kg^{-1}. It should be noted that all studied profiles had the highest CEC in the topsoil (Table 3) where SOM was accumulated.

The BS in soils containing carbonate rocks (Profiles 1, 2, 3) as well as in Profile 4, and soils with metallurgical wastes (Profiles 11, 12, 13), was higher than 94.6 %. BS was much lower in soils with non-carbonate igneous and metamorphic rocks (Profiles 5–10). In the mineral horizons, BS averaged 16.5 %, while in the organic horizons this was 54.8 %. Soils from the Pyszniańska Valley had an average BS of 59.0 % (Table 3).

3.4. Soil magnetic susceptibility

The magnetic susceptibility of the investigated soils ranged from 7 to 10486 × 10^{-8}·m^3·kg^{-1} (Table 2). The highest magnetic susceptibility values were recorded in the Kościeliska Valley in the vicinity of the old steelworks (Profile 11 and 12). Relatively high magnetic susceptibility (up to 91 × 10^{-8}·m^3·kg^{-1}) was characteristic for Profiles 1 and 2 from Huciańskie Banie (where Mn and Fe ore mining took place) and Profile 13 in Kuźnice (old metal steelwork) (up to 128 × 10^{-8}·m^3·kg^{-1}). In the remaining sites (Profiles 3–10), the χ value did not exceed 39 × 10^{-8}·m^3·kg^{-1} (Table 2). In general, soils of Profiles 1–10 and 13 were characterised by higher magnetic susceptibility in the topsoil (avg. 40 ×

10^{-8}·m^3·kg^{-1}) than in the subsoils (avg. 15 × 10^{-8}·m^3·kg^{-1}), with the exception of the Profiles 11 and 12, where the profiles were characterised by a high variability of magnetic susceptibility throughout the soil profiles.

3.5. Soil mineral composition based on XRD analyses

The predominant minerals in Profiles 1 and 2 were calcite and quartz (Table 4). There were also mica and feldspars (albite and orthoclase) present in these profiles. The soils of this area were also characterised by the presence of hematite. Clay minerals (most likely smectite or vermiculite) were found throughout the profile. In Profile 3, at the mouth of the Kościeliska Valley, dolomite was present in addition to a high contribution of quartz. Albite was recorded in the lowermost horizon of this profile.

Table 4
Mineral composition of the soil fine earth (<2 mm) based on powder XRD analyses.

Soil profile	Horizon	Depth (cm)	Mineral phases
1	Oi	0–1	–
	AC1	1–5	Cal, Qz, CM, Mca, Hem, Ab
	AC2	5–15	Cal, Qz, Mca, CM, Ab, Hem, Or
	C	15–35	Cal, Qz, Ab, CM, Mca, Hem
	2C	35–60	Qz, Cal, Mca, CM, Hem
P2	Oi	0–1	–
	AC1	1–25	Cal, Qz, CM, Mca, Ab, Hem
	AC2	25–45	Cal, Qz, Mca, CM, Ab, Hem
	AC3	45–65	Cal, Qz, Mca, CM, Ab, Hem
	2C	65–90	Qz, Cal, Ab, CM, Mca, Hem
P3	Oe	0–6	–
	O/C	6–25	Qz, Dol
	AC	25–40	Qz, Dol
	BC	40–60	Qz, Dol, Ab
P4	Oi	0–1	–
	A	1–13	Qz, Mca, Or, Ab, Chl, Dol?, Py?
	C1	13–35	Qz, Mca, Or, Ab, Chl, Jrs?, Dol?
	C2	35–60	Qz, Mca, Or, Ab, Chl, Dol?
P5	Oe	0–3	–
	Oa	3–10	–
	A	10–15	Qz, Mca, Ab
	Bw	15–20	Qz, Mca, Ab, Chl, Py?, Jrs?
	C	20–45	Qz, Mca, Ab, Chl, Jrs?, Py?
P6	Oe	0–2	–
	Oa	2–10	–
	ABw	10–20	Qz, Mca, Ab, Chl, Or
	C	20–65	Qz, Mca, Ab, Or, Chl, Jrs
P7	Oe	0–2	–
	AC	2–15	Qz, Ab, Mca, Chl, Or
	C	15–50	Qz, Mca, Ab, Chl, Or
P8	Oe	0–4	–
	AC	4–15	Qz, Mca, Ab, Jrs
	C1	15–35	Qz, Mca, Ab, Or, Jrs
	C2	35–55	Qz, Mca, Ab, Or, Jrs?
P9	Oi	0–2	–
	AC	2–10	Qz, Mca, Ab, Jrs
	C1	10–40	Qz, Mca, Ab, Jrs, Chl
	C2	40–80	Qz, Mca, Ab, Jrs
P10	Oi	0–1	–
	AC	1–10	Qz, Mca, Ab, Chl
	C1	10–50	Qz, Mca, Ab, Chl, Or
	C2	50–70	Qz, Mca, Ab, Chl, Or, Jrs
P11	Oi	0–1	–
	A	1–15	Qz, Mag, Ab, Fa, Hem
	C1	15–30	Qz, Mag, Ab, Kln, Mca, Fa, Hem
	C2	30–45	Qz, Mag, Fa, Hem, Ab
	C3	45–60	Qz, Mag, Wüs, Hem, Fa, Ab
P12	Oi	0–1	–
	A	1–20	Qz, Mag, Ab, Hem, Fa, CM, Mca, Kln
	C1	20–28	Qz, Ab, Or, Mca,
	2C	28–50	Qz, Mag, Wüs, Hem, Fa, Ab
	3C	50–60	Qz, Mca, Gth, Cal, Ab
	4C	60–75	Qz, Ab, Mca, Or, Chl?
P13	Oi	0–1	–
	AC	1–15	Qz, Ab, Or, Mca, Chl
	2C	15–25	Qz, Ab, Mca, Or, Chl, Dol, Cal

Explanations: – not analysed. Mineral symbols: Ab – albite, Cal – calcite, Chl – chlorite, CM – clay minerals (smectite, vermiculite or mixed-layer clays), Dol – dolomite, Fa – fayalite, Gth – goethite, Hem – hematite, Jrs – jarosite, Kln – kaolinite, Mag – magnetite, Mca – mica, Or – orthoclase, Py – pyrite, Qz – quartz, Wüs – wüstite.

The dominant mineral in Profiles 4–10 was quartz, accompanied by mica and feldspars (orthoclase and albite) (Table 4). Some soil horizons contained admixtures of chlorite. Jarosite was also identified in all these soils but not in all soil horizons. The occurrence of pyrite was likely in certain horizons of Profile 4 and 5. Admixture of some amphibole was found in the subsoil of Profile 7. Profile 4 probably contained an admixture of dolomite.

The Profiles 11 and 12 from the area of abandoned smelter at the Kościeliska Valley had diverse mineral composition throughout soil profiles. Quartz was predominant in both profiles (Table 4). Magnetite, hematite and fayalite were found in Profile 11 as well as in A and 2C horizons of Profile 12. Feldspars (albite and orthoclase) were recorded at all profile depths. Mica occurred in individual horizons of Profile 11 and 12 (Table 4). Clay minerals (smectite and/or vermiculite, as well as kaolinite and chlorite) were identified in a few horizons of both profiles. Moreover, wüstite was found in C3 horizon of Profile 11 and 2C horizon of Profile 12. Profile 12 was also characterised by the presence of goethite and calcite in horizon 3C (50–60 cm). Profile 13 in Kuźnice contained quartz, feldspar, mica and chlorite, whereas dolomite and calcite were also found in 2C horizon.

3.6. Microscopic observations

Petrographic microscope observations showed the arrangement of soil components (rock fragments, groundmass) and their mineral composition. The analyses revealed that the major soil constituents are rock fragments of which petrographic features and mineral composition differed between soil profiles depending on parent material (Fig. 3). The investigated soil's fine material was dispersed between rock fragments. In Profiles 1 and 2, the soil skeleton consisted of carbonate rocks (Fig. 3A and 3B), Profile 4 contained both carbonate and non-carbonate rocks (Fig. 3C) while Profiles 5–10 contained non-carbonate igneous (granites) and metamorphic (gneisses) rocks (Fig. 3D–3F). Profiles 11–13 were characterised by the presence of slag and charcoal fragments (Fig. 3G and 3H).

The groundmass occurring in the form of soil aggregates between rock fragments was characterised mainly by complex, granular and intergrain micro-aggregate microstructure and complex or single packing voids (Fig. 3). The studied soils had crumb aggregates or sub-angular blocks with undifferentiated birefringence fabric (b-fabric). Aggregates consisted of fine material rich in humified SOM occurring most likely as organo-mineral associations (not shown). In the ABw horizon of Profile 6, organic residues such as plant roots occurred in greater quantity.

3.7. Total concentrations of major elements

In general, Si was a predominant major element in the studied soils (up to 66.3 % of SiO_2) (Fig. 4; Table S1). In soils with aluminosilicate parent materials and in historical smelting areas (Profiles 4–13), Al was also a significant element. In the chemical composition of Profiles 4–10, there were also generally higher K contents than in the other soils. The soils of the areas of former metallurgical activity were characterised by a very high variability in chemical composition within the profile. In addition to Si and Al, a high proportion of Fe occurred (Fig. 4) in the chemical composition of Profiles 11 and 12. The highest contents of Mg and Ca were recorded in soils developed from carbonate parent materials (Profiles 1–3). High Ca contents were also detected in Profile 13, where there was a carbonate-containing subsoil below the slag layer (Fig. 4). A substantial contribution of Mn was recorded in Profiles 1 and 2 developed on a heap near a historical Fe and Mn ore mine at

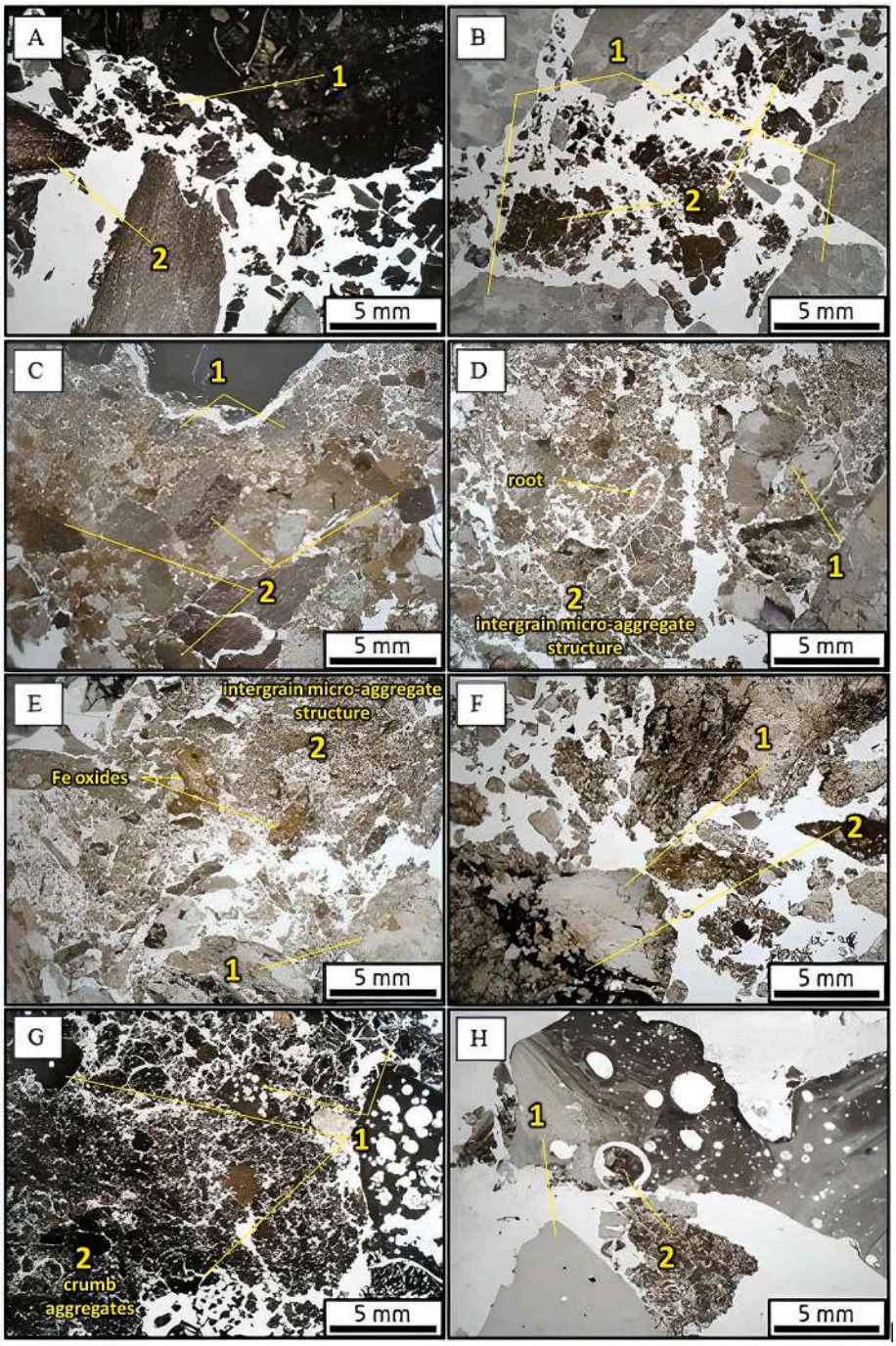


Fig. 3. Optical microscope images (PPL – transmitted light). A – carbonate rocks (1) and rocks containing Fe and Mn oxides (2), Profile 1, 2C2 horizon. B – carbonate rocks (1) and microaggregates built of soil micromass (2), Profile 2, AC1 horizon. C – A mixture of different kind of rock fragments including carbonate rocks (1) and rocks containing hematite (2), Profile 4, C1 horizon. D – Fragments of granites (1) and soil microaggregates (2), Profile 6, ABw horizon. E – Fragments of granites (1) and soil microaggregates (2), Profile 8, AC/C1 horizon. F – Fragments of granites (1) containing Fe oxides (2), Profile 9, AC horizon. G – Metallurgical slag fragments (1) in a black soil material rich in charcoals (2), Profile 11, C2 horizon. H – Metallurgical slag fragments (1) and soil microaggregates (2), Profile 13, AC horizon.

Huciańskie Banie.

4. Discussion

4.1. General soil characterization and the specific features of Tatra-Mountain Technosols

Soil development in the Tatra Mountains is influenced by (1) geological background, (2) specific geomorphological settings (high and steep slopes with differing exposition, dynamic morphogenetic processes), (3) specific climatic conditions (low temperatures, high precipitation) and altitude-zone vegetation characteristic of mountain ecosystems, (4) time as well as (5) limited but influential human activities (Komornicki and Skiba, 1996). In the alpine and subalpine meadow zones, geomorphological factors such as debris flows are crucial for soil formation, whereas in the dwarf pine (*Pinus mugo*) zone and upper alpine forest zone with spruce (*Picea abies*), climate and vegetation have a stronger influence on pedogenesis (Drewnik, 2008). The soils of the lower alpine forests are mainly shaped by parent material.

The most important soil-forming processes occurring in the Tatra

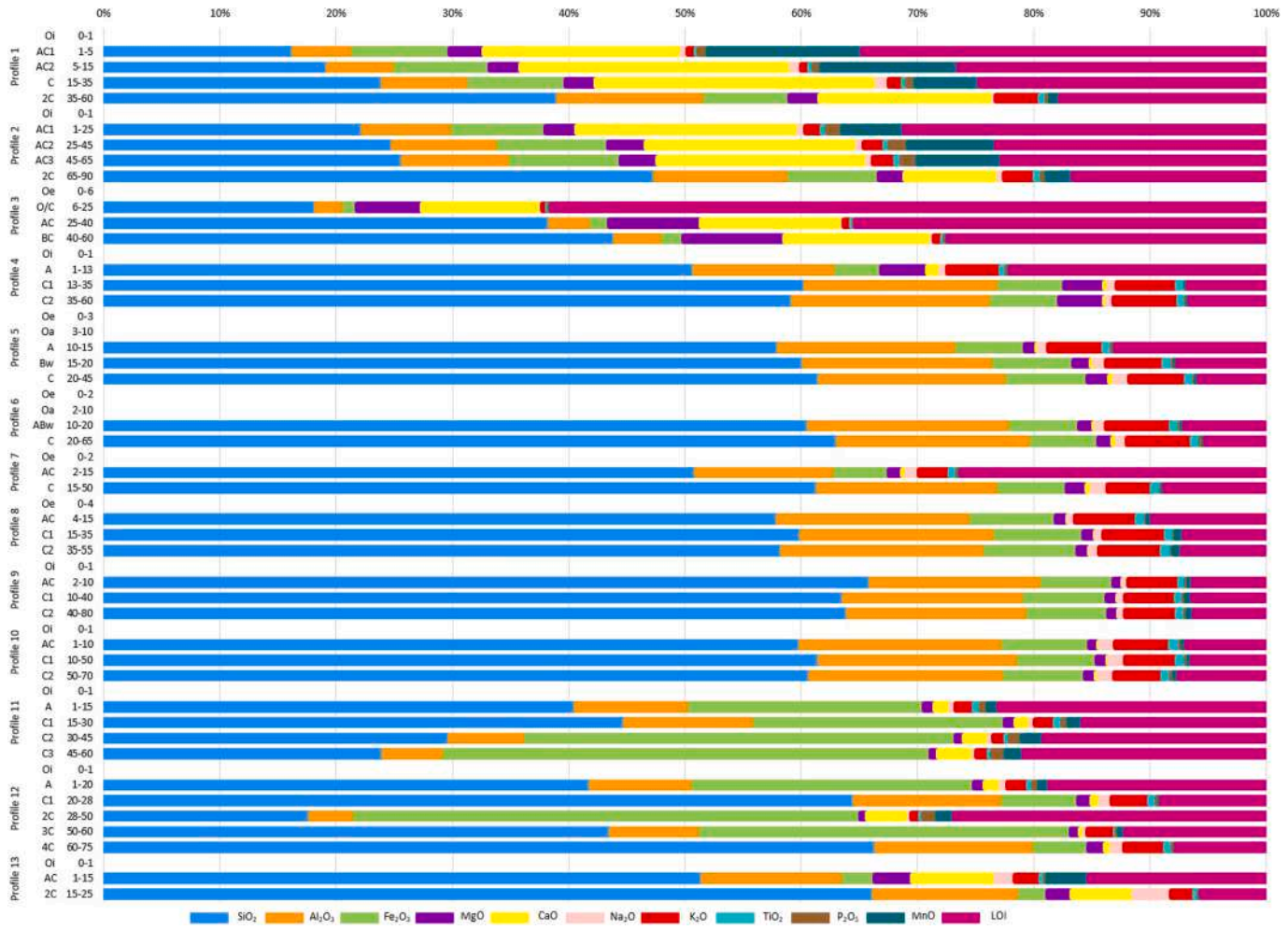


Fig. 4. Percentage share of major elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, Mn) and LOI in the studied soil profiles. Total concentrations of elements and LOI are shown in Table S1 (supplementary materials).

Mountains are (1) podzolization (takes place on regoliths of non-carbonate igneous and metamorphic rocks as well on post-glacial moraines), (2) accumulation of soil organic matter (takes place commonly regardless the parent material, in particular in the zone of dwarf pine and in the upper alpine forest with spruce, in land depressions and in the valleys where organic soils can be formed) and (3) brownification (this takes place mostly on thick regolith covers on mountain foothills, but also on carbonate rock outcrops) (Komornicki and Skiba, 1996; Skiba, 2007; Miechówka and Drewnik, 2018). Based on the results obtained (i.e., soil morphology and properties), one can conclude the soil-forming processes in the studied Technosols are not advanced. The studied Technosols exhibit features of the initial soils having O and A horizons (containing SOM) in the topsoil and C horizons (comprising parent rock materials) in the subsoil. The exceptions are Profiles 5 and 6 from Pyszniańska Valley, where Bw horizons were distinguished. Therefore more advanced soil-forming process (podzolization or brownification) seem to influence the development of these soils. The formation of these horizons is most likely related to the long duration of soil-forming processes in that site discussed below.

Studies on Technosols properties, genesis and evolution are still ongoing worldwide (Néel et al., 2003; Charzyński et al., 2013; Huot et al., 2015; Santini and Fey, 2016; Uzarowicz and Skiba, 2011; Uzarowicz et al., 2017). All these studies focus on Technosols in lowland or highland urban and post-industrial areas with little research on high-mountain environments like the Tatras. Recent publications about high mountain soils under anthropogenic influence focus on soil contamination (Ciarkowska and Miechówka, 2022; Guillevic et al., 2023). However, there is a need to study the influence of high-mountain environmental conditions and their effect on Technosol genesis. To the best author's knowledge, the present paper is one of the first attempts to study the genetic aspects of high-mountain Technosols.

Until now, researchers paid little attention to Tatra-Mountain Technosols. However, Spolic Technosols in the Tatra Mountains are a specific type of post-industrial soils formed from post-mining and smelting metallurgical wastes. Moreover, these soils have not been indicated on Tatra-Mountain soil maps (Skiba et al., 2015) due to their limited and dispersed occurrence. Historically, Tatra-Mountain mines and smelting areas were small in character rather than being part of large industrial plants (Jost, 1962). Nevertheless, it is important to add Technosols to Tatra-Mountain soil maps and treat Technosols as a soil group contributing to the area's soil diversity.

The soil-forming factors that influence the development of Technosols include similar factors to native mountain soils i.e., parent material, biota (plants, animals, microorganisms), climatic conditions (related to altitudinal zonality in mountains), relief and morphogenetic processes, time and human activity (Howard, 2017). The anthropogenic substrates (e.g., mine and metallurgical wastes) that make up Technosols constitute the soil parent material that determines most of their properties. The climate in which Technosols form can affect the rate of soil-forming processes and the development of soil horizons. Consequently, climatic conditions shape biota, the presence and activity of which can influence the development of Technosols through their

impact on the rate of SOM accumulation and decomposition (Drewnik, 2006; Frouz et al., 2008; Wasak, 2014; El Mderssa et al., 2023). Technosols can form on flat surfaces or slopes and their relief can affect the movement of water and sediment, which can impact the development of soil horizons (Woś and Pietrzykowski, 2020). The time of Technosol formation can also affect the degree of advancement of soil-forming processes expressed in soil morphology (e.g., occurrence of B horizons). Soils that have been forming for a longer period tend to have more distinct soil horizons and a higher degree of development (Skiba et al., 2004).

The comparison of pedogenetic aspects between the Technosols in lowland/highland and high-mountain areas is difficult because of a lack of data for the latter. Although the literature about pedogenesis of Technosols in areas of historical mining and smelting in lowlands or highland areas is available (Huot et al., 2015; Ivanov et al., 2009; Uzarowicz and Skiba, 2011), data on the development and evolution of mountain Technosols is scarce. The main similarities seem to be that both lowland/highland and high-mountain Technosols occur in the isolated patches where industrial waste was deposited. These have different parent materials than the surrounding areas (Adamczyk, 1965; Kierczak et al., 2009; Pietrzykowski et al., 2011; Swęd et al., 2022). Post-industrial areas both in lowland/highland (Karczewska et al., 2018; Pająk et al., 2018; Potysz et al., 2019; Tarnawczyk et al., 2021; Uzarowicz et al., 2020a) and high-mountain areas (Ciarkowska and Miechówka, 2022) are often highly contaminated with potentially toxic trace elements. On the other hand, the differences between Technosol pedogenesis in lowland/highland areas and high mountains most likely reflects the geoecological conditions related to relief, altitude, climatic conditions and plant cover. These differences may lie in different soil microbial activity in lowlands/highlands and high mountains; however, that issue should be examined in detail in the future.

4.2. *Historical human activity and parent rock as the major soil-forming factors*

The crucial soil-forming factor responsible for the formation of the studied Technosols was the human activity in the past. There can be no disputing that without mining and smelting as well as deposition of industrial of mining and metallurgical wastes on the land surface, the examined Technosols would not exist. Human activity affects the nature, quantity and distribution of the anthropogenic materials making up the soil substrate.

The type of parent rock is the main soil-forming factor controlling the majority of soil properties (Huang et al., 2011). Its influence on soils can be complex and can vary depending on the specific geological background. Parent-rock mineral and chemical composition determines soil properties (e.g., pH), availability of nutrients as well as soil structure and drainage. The parent rock can also affect the rate of weathering and erosion, leading to the development of different soil horizons (Blume and Schwertmann, 1969; Wilson, 2004).

A number of previous studies have shown that parent rock is the most important soil-forming factor controlling the variability and properties of Tatra-Mountain native soils (Komornicki and Skiba, 1996; Miechówka et al., 1997; Skiba et al., 2004; Wasak-Sęk, 2017). The results presented herein indicate this is also true for the Technosols there. The type of parent material determined the features of the studied Technosols like soil physical properties (soil texture), chemical (content of carbonates in soils, soil pH) and sorption properties (e.g. CEC and BS), magnetic susceptibility as well as mineral and chemical composition (Fig. 4; Tables 2–4, S1).

The studied Technosols can be divided into three groups according to the nature of the parent material: group I – Technosols developed from mine wastes derived from carbonate rocks (Profiles 1–3); group II – Technosols developed from mine wastes derived from aluminosilicate igneous and metamorphic rocks (Profiles 5–10), and group III – Technosols developed in historical smelting areas and containing metallurgical wastes (Profiles 11–13). Profile 4 had the properties of soils representing both group I and II (Fig. 5). The PCCA analysis shows the diversity of the studied Technosols is mostly determined by three principal components (Fig. 5): the first explains 53.3 % of the variability of the data and is related with SiO_2, Al_2O_3 and CaO concentration, EB, pH_{H2O} and carbonate content. This principal component clearly distinguished the above mentioned soil groups. The second principal component explains 20.9 % of the variability of the data and is related with magnetic susceptibility and Fe_2O_3 concentration. The third explains 10.2 % of data variability and is related to EA.

Group I Technosols are characterized by the high contribution of carbonate rock fragments, high pH_{H2O} (7.5 on average), carbonate content (21 % on average), relatively high CEC (36 cmol(+)•kg^{-1} on average) and BS (99.7 % on average). The soils' mineral composition is dominated by calcite, quartz, mica, hematite and dolomite. On average, concentrations of major elements can be arranged as follows: Si > Ca > Al > Fe > Mn > Mg > K > P > Na > Ti. Parent-material carbonates in Profiles 1–3 affect soil properties and chemical composition, which was clearly detected by PCCA analysis (Fig. 5). All these soils have very much in common with 'rendzina soils' typical of carbonate bedrock (Miechówka and Drewnik, 2018). Some are enriched in Fe and Mn, in particular in areas of historical Fe- and Mn-bearing ore mining (Jach and Dudek, 2005).

Group II Technosols developed from mine wastes comprising non-carbonate igneous or metamorphic rocks (Profiles 5–10) are characterized by low pH_{H2O} (4.3 on average), lack of carbonates, low CEC (6 cmol(+)•kg^{-1} on average in mineral horizons), low BS (24,7% on average in mineral horizons) and relatively low χ (avg. 16 × 10^{-8}·m^3·kg^{-1} on average). Mineral composition of these soils is dominated by quartz, mica, albite, orthoclase and chlorite. On average, the major elements can be arranged as follows: Si > Al > Fe > K > Mg > Na > Ti > Ca > Mn > P. Group II Technosols can be very well distinguished in Fig. 5 based on the first principal component. The low pH and relatively high content of SiO_2, Al_2O_3, and K_2O in group II Technosols is strictly related to soil-parent material mineral and chemical composition. These Technosols have the features of native soils developed from granites and gneisses as well as non-carbonate glacial moraines occurring mostly in the foothills and valleys of the Eastern (High) Tatra Mountains (Drewnik et al., 2008).

Group III includes Technosols developed in historical smelting areas and has some common features, for example high pH (6.4 on average), relatively high CEC (25 cmol(+)•kg^{-1} on average in mineral horizons) and high BS (99.1 % on average) as revealed by PCCA analysis (Fig. 5). Features of this kind are characteristic for soils developed from metallurgical slags and thermal power station ash (Kierczak et al., 2008; Potysz et al., 2015; Uzarowicz et al., 2017; Uzarowicz et al., 2018a, 2018b). On the other hand, a typical attribute of that group of Technosols is the great diversity of mineral and chemical composition. One particular mineralogical feature is the occurrence of soil layers enriched in metallurgical slags containing amorphous phases (slags), magnetite, olivines (e.g. fayalite), wüstite and hematite. High χ was typical of soils from group III. In particular, very high χ (3565 × 10^{-8}·m^3·kg^{-1} on average) is typical of soil layers rich in metallurgical wastes. The profiles of these Technosols are also very diverse in chemical composition; however, the following general pattern of major elements can be determined as Si > Fe > Al > Ca > K > Mg > Mn > Na > P > Ti. A typical feature of these soils is the high Fe concentration, which is related to the occurrence of Fe-rich minerals like magnetite, fayalite, wüstite and hematite.

Profile 4 shared features of both group I and II (Fig. 5). That soil had a pH of 6.6 on average, lack of carbonates, as in group II, as well as moderate CEC (15 cmol(+)•kg^{-1} on average), high BS (99.6 on average) and generally low χ (avg. 13 × 10^{-8}·m^3·kg^{-1}). That soils' mineral composition is dominated by quartz, mica, orthoclase, albite and chlorite. On average, the concentrations of the major elements can be arranged as follows: Si > Al > Fe > K > Mg > Ca > Ti > Na > P > Mn.

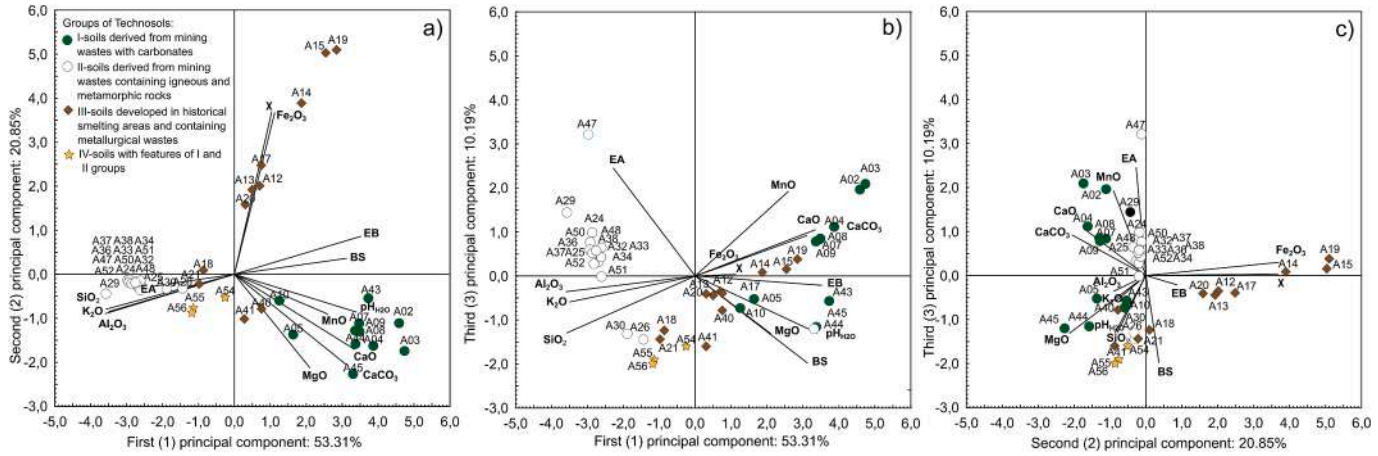


Fig. 5. Principal Component and Classification Analysis (PCCA) of studied Technosols in the Tatra Mountains (coordinates of the principal components and explanation of symbols of soil samples are given in Table S2 and S3 (supplementary materials).

The studied parent material revealed diverse susceptibility to weathering. Mine-waste Technosols derived from carbonate rocks (Profiles 1–3) contained calcite or dolomite, which are relatively soluble in the environment (Zamanian et al., 2016). On the other hand, Profiles 5–10 were developed from parent materials containing granites and gneisses, the minerals of which are relatively resistant to weathering. Some rocks contained sulphides, which are highly susceptible to weathering in soil environments (Néel et al., 2003; Uzarowicz and Skiba, 2011). Metallurgical wastes occurring in Profiles 11–13 contained a variety of mineral phases that are mostly quite resistant to weathering (Potysz et al., 2015), although some elements (e.g., Cu) were released during weathering and formed secondary minerals (e.g., malachite). Formation of pedogenic Cu carbonates was reported in mine-waste Technosols near historical Cu mines (Uzarowicz et al., 2024).

Investigated Technosols' magnetic susceptibility was strongly influenced by the presence of magnetic phases (mainly Fe oxides like magnetite or hematite) inherited from the soil parent materials. The highest magnetic susceptibility was measured in soils containing metallurgical slags (Profiles 11 and 12) (Table 2). These soils were enriched in technogenic magnetite particles that contributed to very high magnetic susceptibility. Investigations of Technosols developed on thermal power station ash disposal sites highlight the significant influence of parent-material magnetic minerals (e.g. magnetite) on soil magnetic properties (Uzarowicz et al., 2021). Magnetic susceptibility is a parameter commonly used to investigate both genetic aspects and the level of soil contamination. Soils can contain different magnetic minerals inherited from the parent material as well as being influenced by climate, vegetation and soil-forming processes (Blume and Schwertmann, 1969). Soil-forming processes can increase topsoil magnetic susceptibility through mineral alteration and organic matter accumulation (Fine et al., 1989, Frankl et al., 2022). In stable soils, magnetic susceptibility tends to increase upwards due to intense near-surface soil-forming processes (Cerdan et al., 2010; Górka-Kostrubiec et al., 2016). Such a feature was also detected in majority of the studied soil profiles (Table 2), however additional magnetometric analyses have to applied to explain higher magnetic susceptibility in the topsoil than in the subsoil of the investigated Technosols in detail.

4.3. *Vegetation as a soil-forming factor controlling topsoil properties*

Vegetation is, apart from parent material, another important soil-forming factor determining the studied Technosols properties. Vegetation plays an important role in the post-mining recovery of Tatra-Mountain soils; once mining ceases, vegetation starts returning to the mined area, which is important for the natural soil regeneration. Trees and other plants help to stabilize the soil and prevent erosion and also promote SOM accumulation. This improves soil properties, increases fertility and supports the growth of plants. Additionally, vegetation helps to recharge mining-area groundwater (Galhardi and Bonotto, 2016). Overall, vegetation has been an essential component of the post-mining recovery process in the Tatra Mountains and was crucial for restoring the natural ecosystem.

The results of this study of post-mining and post-smelting soils indicate that the vegetation and plant-derived SOM mostly shapes the topsoil properties of the studied Technosols. As a result of the development of vegetation in post-mining and post-smelting areas in the Tatra Mountains, SOM has been accumulated in the studied soil-profile topsoil (Fig. 2). Investigated-soil TOC content reached up to 48 % and TN concentration varied between 0.06 and 2.06 % (Table 2). Generally, SOM-related TN concentration was higher in the topsoil than subsoil. Post-mining and post-smelting site vegetation provided organic matter that was transformed into humus of mor and moder type. SOM accumulation influenced soil structure (formation of aggregates composed of organo-mineral compounds, Fig. 3) and soil pH. For example, the accumulation of spruce (e.g. at Żleb pod Banie) and dwarf pine needles (e.g. at Banisty Żleb) caused an acidic reaction regardless of the soil's parent material (Table 2). Moreover, SOM accumulated in the topsoil influenced soil sorption properties (Table 3). This was clearly visible in the surface soil horizons, where CEC was higher in comparison with the subsoil. SOM humic compounds show strong sorption properties that enhance soil CEC (Wasak and Drewnik, 2016; Salami et al., 2024). Furthermore, SOM accumulation may also have an impact on soil microbial activity and diversity though that is a topic for future studies.

The Fig. 4 shows the major-element and LOI variation in the soil profiles studied. The element-content differences are obviously related to bedrock mineral composition. In contrast, the LOI was higher in soil horizons with a high contribution of organic matter (both soil organic matter in the O horizons and organic matter in charcoal form in the soils containing slag) and carbonates or hydrated minerals.

4.4. *Climate, relief, water and time as soil-forming factors controlling soil properties and genesis*

In alpine environments, including the Tatra Mountains, altitude influences climatic conditions and defines the climate-plant zonality (Skiba, 1977). Climate affects the vegetation cover, which in turn influences soil properties as described above. The effect of climate and vegetation on soils can be observed on the slopes of Ornak. Profiles 7 and 8 (Pod Banie Couloir) as well as Profiles 9 and 10 (Banisty Couloir) were located in different climate-plant zones (Table 1). The former soils were covered with spruce forest and largely mosses (*Bryophyta* sp.), while the latter were dominated by *Pinus mugo* shrubs. All soils (Profiles 7–10)

contained similar TOC contents in O horizons (Profiles 9 and 10 showed a little higher TOC concentrations). However, in Profiles 7 and 8, the A horizons were noticeably richer in TOC than A horizons from Profiles 9 and 10 (Table 2). Moreover, the C/N ratios were lower in the former than latter soils. Features like this are related to differences in the SOM-decomposition rate, which is slower above the upper-forest zone in Tatra Mountain soils (Drewnik, 2002, 2006). Research regarding the rate of cellulose decomposition shows this process is mainly influenced by climatic and plant factors, while the geological substrate is much less influential (Drewnik, 2008).

Another important soil-forming factor in the Tatra Mountains are the geomorphological settings (relief) affecting soils e.g., through slope inclination and exposure (Drewnik, 2008). Although the slope inclination influences the intensity of erosion, the effects of water erosion were not observed in the immediate surroundings of the studied soil profiles. Vegetation cover, even on steeper slopes, was effective in protecting the land surface against erosion. Slope exposure and amount of solar radiation influences microclimatic conditions, which in turn affects the range of mountain climatic-plant zones (Komornicki and Skiba, 1996). Based on the results obtained, the influence of climatic conditions and relief on the studied soils are indirect. Climate and geomorphological settings determine vegetation cover, which in turn shapes soil properties.

Water did not determine the investigated Technosols' properties. All studied soils were well aerated and located in well drained sites. No traces of gleyic processes were found (Fig. 2).

The time of soil formation is also a factor controlling soil properties. In the case of the investigated soils, the influence of time is difficult to determine, as other factors such as bedrock, relief, climate-dependent vegetation, through their determining contribution to the formation of soil properties, make assessment difficult. However, the profiles with Bw horizons were located in Pyszniańska Valley, on the oldest sites, where mining was carried out in the 15th Century (at the other sites, mining mainly took place in the 18th and 19th Centuries). Therefore, the formation of Bw horizons may be related to a long pedogenesis period.

5. Conclusions

Soil studies in the historical mining and smelting areas of the Tatra Mountains have revealed the long-lasting and particular impacts of these activities on Technosol properties. These soils are weakly developed soils characterized by high diversity of properties, varying in parent material (mine wastes, metallurgical wastes), vegetation cover as well as elevation a.s.l. (determining climate-plant altitudinal zone) and landform. The duration of soil formation also differed among the studied Technosols.

The most important factors controlling Technosol origin and properties are past human activity, parent material and vegetation. Anthropogenic factors associated with human mining and metallurgical activities had a direct and decisive impact on the studied Technosol origin. Parent material determined majority of soil properties (pH, content of carbonates, sorption properties), magnetic susceptibility, mineral and chemical composition.

Based on the nature of parent material, the studied Technosols can be divided into three groups: group I comprises Technosols developed from mine wastes constituted by carbonate rocks, group II includes Technosols developed from mine wastes derived after non-carbonate igneous and metamorphic rocks and group III comprises Technosols developed in historical smelting areas and containing metallurgical wastes. All these groups are characterized by different soil properties, mineral and chemical composition.

Vegetation that varied with altitude and geomorphological settings promoted soil organic matter accumulation in the topsoil which in turn influenced soil properties in the surface horizons (e.g., pH, content of total organic carbon and total nitrogen, sorption properties).

Other soil-forming factors controlling the studied Technosol properties were relief, altitude-related climatic conditions, water conditions and time of soil formation. Climatic conditions and relief determine the studied Technosols properties indirectly and it is not as pronounced as in the case of human activity, parent material and vegetation. Water only had a limited influence on the studied Technosols as they were located in well-drained areas.

The lengthy soil-formation period (a few centuries) of some studied Technosols led to the formation of weakly developed Bw horizons within soil profiles. This indicates that the progress of soil-forming processes in post-mining areas in the Tatra Mountains can transform Technosols into more developed soils.

CRediT authorship contribution statement

Magdalena Tarnawczyk: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Łukasz Uzarowicz:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Wojciech Kwasowski:** Writing – review & editing, Validation, Supervision, Methodology, Investigation. **Beata Górka-Kostrubiec:** Writing – review & editing, Validation, Methodology, Investigation. **Artur Pędziwiatr:** Writing – review & editing, Validation, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Science Centre, Poland, under research project no. 2021/41/N/ST10/03129; and the Polish Ministry of Education and Science (subvention for the Doctoral School of the Warsaw University of Life Sciences – SGGW). The publication was (co)financed by Science Development Fund of the Warsaw University of Life Sciences – SGGW. Maria Król and Magdalena Sitarz (Tatra National Park) as well as Arletta Kochańska-Jeziorska are acknowledged for their help during the field works and in finding the literature related with the topic. Mr. Emil Tchorek improved the English.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2024.108521.

References

Adamczyk, B., 1965. Secondary transformations of the soil and plant cover in the northwestern region of the Świętokrzyskie Mts. formerly under mining exploitation. Roczniki Gleboznawcze – Soil Science Annual 15 (supl.), 437–442. (in Polish with English abstract).

Bąk, K., 1992. Possibilities of Scheibler method application in researches on calcium carbonate content in solid carbonate rocks. Prace Geograficzne 14, 131–139.

Blume, H.P., Schwertmann, U., 1969. Genetic evaluation of profile distribution of aluminum, iron, and manganese oxides. Soil Sci. Soc. Am. J. 33, 438–444. https://doi.org/10.2136/sssaj1969.03615995003300030030x.

Brogowski, Z., Czerwiński, Z., 2016. Materiały do ćwiczeń z gleboznawstwa. Część II, Wydawnictwo SGGW, Warszawa in Polish.

Cerdan, O., Govers, G., le Bissonnais, Y., Van Oost, K., Poesen, J., Saby, N., Gobin, A., Vacca, A., Quinton, J., Auerswald, K., Klik, A., Kwaad, F.J.P.M., Raclot, D., Ionita, I., Rejman, J., Rousseva, S., Muxart, T., Roxo, M.J., Dostal, T., 2010. Rates and spatial variations of soil erosion in Europe: A study based on erosion plot data. Geomorphology 122, 167–177. https://doi.org/10.1016/j.geomorph.2010.06.011.

Charzyński, P., Hulisz, P., Bednarek, R.M., 2013. Technogenic soils of Poland. Polish Society of Soil Science, Toruń, Poland.

Ciarkowska, K., Miechówka, A., 2022. Identification of the factors determining the concentration and spatial distribution of Zn, Pb and Cd in the soils of the non-forest Tatra Mountains (southern Poland). Environ. Geochem. Health 44, 4323–4341. https://doi.org/10.1007/S10653-022-01201-3.

Dmytrowski, P., Kicińska-Świderska, A.J., 2006. Following the signs of the old mining operations in the valleys of the Tatra Mts. Kościeliska and Chochołowska. Geoturystyka 2, 41–48 in Polish with English abstract.

Drewnik, M., 2002. Rate of organic matter decomposition and humus horizons in the Tatra soils. In: Borowiec, W., Kotarba, A., Kownacki, A., Krzan, Z., Mirek, Z. (Eds.), Changes of the Nature Environment of the Tatra Mountains. Kraków, Polskie Towarzystwo Przyjaciół Nauk o Ziemi, pp. 101–106.

Drewnik, M., 2006. The effect of environmental conditions on the decomposition rate of cellulose in mountain soils. Geoderma 132, 116–130. https://doi.org/10.1016/j.geoderma.2005.04.023.

Drewnik, M., 2008. Geomorphological modalities for the development of soil cover in mountainous areas (using the Tatra Mountains as an example). Wydawnictwo Uniwersytetu Jagiellońskiego, Kraków, Poland.

Drewnik, M., Felisiak, I., Jerzykowska, I., Magiera, J., 2008. The Tatra Mts – rocks, landforms, weathering and soils. Geoturystyka 2, 51–74.

El Mderssa, M., Malki, F., Ikraoun, H., Abbas, Y., Elmalki, M., Nassiri, L., Ibijbijen, J., 2023. Stability of organic matter in forest soils of the middle Central Atlas: Extraction by biochemical fractionation. Soil Sci. Annu. 74, 169154. https://doi.org/10.37501/soilsa/169154.

Fidelus-Orzechowska, J., Gorczyca, E., Bukowski, M., Krzemień, K., 2021. Degradation of a protected mountain area by tourist traffic: case study of the Tatra National Park, Poland. J. Mountain Sci. 8, 2503–2519. https://doi.org/10.1007/s11629-020-6611-4.

Fine, P., Singer, M.J., La Ven, R., Verosub, K., Southard, R.J., 1989. Role of pedogenesis in distribution of magnetic susceptibility in two California chronosequences. Geoderma 44, 287–306. https://doi.org/10.1016/0016-7061(89)90037-2.

Frankl, A.L., Maxbauer, D.P., Savina, M.E., 2022. Linkages between soil organic matter and magnetic mineral formation in agricultural fields in southeastern Minnesota, USA. Geoderma 406, 115466. https://doi.org/10.1016/j.geoderma.2021.115466.

Frouz, J., Prach, K., Pižl, V., Háněl, L., Starý, J., Tajovský, K., Materna, J., Balík, V., Kalčík, J., Řehounková, K., 2008. Interactions between soil development, vegetation and soil fauna during spontaneous succession in post mining sites. Eur. J. Soil Biol. 44, 109–121. https://doi.org/10.1016/j.ejsobi.2007.09.002.

Galhardi, J.A., Bonotto, D.M., 2016. Hydrogeochemical features of surface water and groundwater contaminated with acid mine drainage (AMD) in coal mining areas: a case study in southern Brazil. Environ. Sci. Pollut. Res. 23, 18911–18927. https://doi.org/10.1007/s11356-016-7077-3.

Górecki, J., Sermet, E., 2012. Hawiarskie szlaki Tatr polskich, Dzieje górnictwa–element europejskiego dziedzictwa kultury. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, Poland.

Górka-Kostrubiec, B., Teisseyre-Jeleńska, M., Dytłow, S.K., 2016. Magnetic properties as indicators of Chernozem soil development. Catena 138, 91–102. https://doi.org/10.1016/j.catena.2015.11.014.

Guillevic, F., Rossi, M., Develle, A.L., Spadini, L., Martins, J.M.F., Arnaud, F., Poulenard, J., 2023. Pb dispersion pathways in mountain soils contaminated by ancient mining and smelting activities. Appl. Geochem. 150, 105556. https://doi.org/10.1016/j.apgeochem.2022.105556.

Howard, J., 2017. Anthropogenic soils. Springer Cham, Switzerland.

Hrouda, F., Kahan, Š., 1991. The magnetic fabric relationship between sedimentary and basement nappes in the High Tatra Mountains, N. Slovakia. J. Struct. Geol. 13, 431–442. https://doi.org/10.1016/0191-8141(91)90016-C.

Huang, P.M., Li, Y., Sumner, M.E., 2011. Handbook of soil sciences: properties and processes. CRC Press, New York.

Huot, H., Simonnot, M.O., Morel, J.L., 2015. Pedogenetic trends in soils formed in technogenic parent materials. Soil Sci. 180, 182–192. https://doi.org/10.1097/SS.0000000000000135.

IUSS Working Group WRB, 2022. World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps, fourth ed. International Union of Soil Sciences (IUSS), Vienna, Austria.

Ivanov, P., Banov, M., Tsolova, V., 2009. Classification of Technosols from Bulgaria using World Reference Base (WRB) for Soil Resources. J. Balkan Ecol. 12, 53–57.

Jach, R., 2002. Traces of historical exploitation of manganiferous ores in the western tatra mountains. Przegląd Geologiczny 50, 1159–1164 in Polish with English abstract.

Jach, R., Dudek, T., 2005. Origin of a Toarcian manganese carbonate/silicate deposit from the Krížna unit, Tatra Mountains, Poland. Chem. Geol. 224, 136–152. https://doi.org/10.1016/j.chemgeo.2005.07.018.

Jahn, R., Blume, H.P., Asio, V.B., Spaargaren, O., Schad, P., 2006. Guidelines for soil description. FAO, Rome, Italy.

Jost, H., 1962. O górnictwie i hutnictwie w Tatrach Polskich. Wydawnictwo Naukowo-Techniczne, Warszawa, Poland.

Kabała, C., Charzyński, P., Chodorowski, J., Drewnik, M., Glina, B., Greinert, A., Hulisz, P., Jankowski, M., Jonczak, J., Łabaz, B., Łachacz, A., Marzec, M., Mendyk, Ł., Musial, P., Musielok, Ł., Smerczak, B., Sowiński, P., Świtoniak, M., Uzarowicz., Waroszewski, J., 2019. Polish soil classification, sixth ed. - Principles, classification scheme and correlations. Soil Sci. Annual 70, 71–97. Doi: 10.2478/ssa-2019-0009.

Karczewska, A., Lewińska, K., Siepak, M., Gałka, B., Dradrach, A., Szopka, K., 2018. Transformation of beech forest litter as a factor that triggers arsenic solubility in soils developed on historical mine dumps. J. Soil. Sediment. 18 (8), 2749–2758. https://doi.org/10.1007/s11368-018-2031-2.

Kierczak, J., Neel, C., Aleksander-Kwaterczak, U., Helios-Rybicka, E., Bril, H., Puziewicz, J., 2008. Solid speciation and mobility of potentially toxic elements from natural and contaminated soils: A combined approach. Chemosphere 73, 776–784. https://doi.org/10.1016/j.chemosphere.2008.06.015.

Kierczak, J., Néel, C., Puziewicz, J., Bril, H., 2009. The mineralogy and weathering of slag produced by the smelting of lateritic Ni ores, Szklary, southwestern Poland. Can. Mineral. 47 (3), 557–572. https://doi.org/10.3749/canmin.47.3.557.

Komornicki, T., Skiba, S., 1996. Gleby. In: Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Przyroda Tatrzańskiego Parku Narodowego. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 215–229.

Kubica, B., Mietelski, J.W., Gołaś, J., Skiba, S., Tomankiewicz, E., Gaca, P., Jasińska, M., Tuleja-Krysa, M., 2002. Concentration of 137 Cs, 40 K, 238 Pu and 239+240 Pu Radionuclides and Some Heavy Metals in Soil Samples from Two Main Valleys from Tatra National Park. Pol. J. Environ. Stud. 11, 537–545.

Kubica, B., Kwiatek, W.M., Stobiński, M., Skiba, S., Skiba, M., Gołaś, J., Kubica, M., Tuleja-Krysa, M., Wrona, A., Misiak, R., Krzan, Z., 2007. Concentrations of 137Cs, 40K radionuclides and some heavy metals in soil samples of Chochołowska Valley from Tatra National Park. Pol. J. Environ. Stud. 16, 723–729.

Lal, R., Stewart, B.A. (Eds.), 2017. Urban Soils. CRC Press, New York.

Miechówka, A., 1989. Geochemical characteristics of Tatra rendzinas formed on dolomites. Cz. I. Ogólna charakterystyka gleb i niektóre dane mineralogiczne. Roczniki Gleboznawcze – Soil Sci. Annu. 40, 83–105.

Miechówka, A., Ciarkowska, K., 1998. Mikromorfologiczne formy próchnicy tatrzańskich rędzin próchnicznych i butwinowych. Zeszyty Problemowe Postępów Nauk Rolniczych 464, 161–168.

Miechówka, A., Drewnik, M., 2018. Rendzina soils in the Tatra Mountains, central Europe: a review. Soil Sci. Annu. 69, 88–100.

Miechówka, A., Gąsiorek, M., Zaleski, T., 1997. Contents of cadmium and nickel in soils and plants on grazed mountain glades in Tatra National Park. Zeszyty Problemowe Postępów Nauk Rolniczych 448, 197–202.

Miechówka, A., Niemyska-Łukaszuk, J., 2004. Content diversity of Zn, Pb and Cd in Lithic Leptosols of the Tatra National Park (Poland). Oecologia Montana 13, 1–5.

Miechówka, A., Zadrozny, P., Mazurek, R., Ciarkowska, K., 2021. Classification of mountain non-forest soils with umbric horizon - a case study from the Tatra Mountains (Poland). Soil Sci. Annu. 72, 134619. https://doi.org/10.37501/soilsa/134619.

Néel, C., Bril, H., Courtin-Nomade, A., Dutreuil, J.P., 2003. Factors affecting natural development of soil on 35-year-old sulphide-rich mine tailings. Geoderma 111, 1–20. https://doi.org/10.1016/S0016-7061(02)00237-9.

Niemyska-Łukaszuk, J., 1977. Characteristics of the humus of some forest soils in the Tatra Mts. Part. II. Fractionary composition of the humus compounds. Roczniki Gleboznawcze –. Soil Sci. Annu. 28, 143–168.

Nyka, J., 1969. Tatry Polskie: przewodnik. Wydawnictwo Sport i Turystyka, Warszawa, Poland.

Oleksynowa, K., Skiba, S., 1977. Characteristics of some cryogenic soils in the Tatra Mts. Roczniki Gleboznawcze – Soil Science Annual 28, 293–312. (in Polish with English abstract).

Oleksynowa, K., Skiba, S., Kania, W., 1977. Introductory investigations on the geochemistry of rendzinas in the Tatra Mts. Roczniki Gleboznawcze – Soil Science Annual 28, 263–275. (in Polish with English abstract).

Ostrowska, A., Gawliński, S., Szczubiałka, Z., 1991. Metody analizy i oceny właściwości gleb i roślin. Instytut Ochrony Środowiska, Warszawa in Polish.

Pająk, M., Błońska, E., Szostak, M., Gąsiorek, M., Pietrzykowski, M., Urban, O., Derbis, P., 2018. Restoration of vegetation in relation to soil properties of spoil heap heavily contaminated with heavy metals. Water Air Soil Pollut. 229, 392. https://doi.org/10.1007/s11270-018-4040-6.

Pansu, M., Gautheyrou, J., 2006. Handbook of Soil Analysis. Mineralogical, Organic and Inorganic Methods. Springer Berlin, Heidelberg.

Paulo, A., 1979. Tatric Mineral Deposits. Przegląd Geologiczny 27, 396–399 in Polish with English abstract.

Paulo, A., Panajew, P., 2006. Iron ore from historical mines of Bobrowiec (Western Tatra Mountains). Geologia 32, 99–115 in Polish with English abstract.

Pawlikowski, M., Walczak, M., Krawiec, A., Wróbel, M., 2014. Microbiological and mineralogical investigation of ores from selected polish deposits. Auxiliary Sci. Archaeol., Preservat. Relics Environ. Eng. 17, 1–28 in Polish with English abstract.

Pawlikowski, M., Wróbel, M., 2013. Rediscovering old mining activities in the Tatra Mountains. Geotourism/geoturystyka 1–2, 37–46. https://doi.org/10.7494/geotour.2013.32-33.37.

Piękoś-Mirkowa, H., Mirek, Z., 1996. Zbiorowiska roślinne. In: Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Przyroda Tatrzańskiego Parku Narodowego. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 237–274.

Pietrzykowski, M., Krzaklewski, W., Piechnik, Ł., 2011. Soil characteristics on afforested areas after calamine mining. Roczniki Gleboznawcze – Soil Science Annual 62(2), 325–334. (in Polish with English abstract).

Polish Soil Classification, 2019. Soil Science Society of Poland, Commission on Soil Genesis, Classification and Cartography. Wydawnictwo Uniwersytetu Przyrodniczego we Wrocławiu, Polskie Towarzystwo Gleboznawcze, Wrocław –Warszawa, Poland.

Potysz, A., van Hullebusch, E.D., Kierczak, J., Grybos, M., Lens, P.N., Guibaud, G., 2015. Copper metallurgical slags–current knowledge and fate: a review. Crit. Rev. Environ. Sci. Technol. 45, 2424–2488. https://doi.org/10.1080/10643389.2015.1046769.

Potysz, A., Pędziwiatr, A., Hedwig, S., Lenz, M., 2019. Rapid metal mobilisation through litter, water and bioweathering as the legacy of historical copper smelting. J. Geochem. Explor. 206, 106364. https://doi.org/10.1016/j.gexplo.2019.106364.

Rate, A.W., 2022. The Future of Urban Soils, in: Rate, A.W. (Eds.) Urban Soils: Principles and Practice, Springer Cham, pp. 399–427.

Salami, O.O., Awotoye, O.O., Adesanwo, O.O., Adebola, S.I., 2024. Humic acid structural characteristics in soils under different land uses in Ilesa, Nigeria. Soil Sci. Annual 75 (2), 189544.
Santini, T.C., Fey, M.V., 2016. Assessment of Technosol formation and in situ remediation in capped alkaline tailings. Catena 136, 17–29. https://doi.org/10.1016/j.catena.2015.08.006.
Sitarz, M., Gołębiowska, B., Nejbert, K., Dimitrova, D., Milovský, R., 2021. Hydrothermal ore mineralization from the Polish part of the Tatra Mts., Central Western Carpathians. Geol., Geophys. Environ. 47, 159–179. https://doi.org/10.7494/geol.2021.47.3.159.
Skiba, S., 1985. Rola klimatu i roślinności w genezie gleb na przykładzie gleb górskich z Tatr Polskich i z gór Mongolii. Zeszyty Naukowe Akademii Rolniczej w Krakowie, Seria Rozprawy Habilitacyjne 99, 1–72.
Skiba, M., 2007. Clay mineral formation during podzolization in an alpine environment of the Tatra Mountains, Poland. Clay Clay Miner. 55, 618–634. https://doi.org/10.1346/CCMN.2007.0550609.
Skiba, S., Drewnik, M., Klimek, M., Kacprzak, A., Żyła, M., 2004. Soil cover in the Carpathian national parks in Poland. Przyroda Człowiek Bóg 1, 115–125 in Polish with English abstract.
Skiba, S., Koreň, M., Drewnik, M., Kukla, J., 2015. Gleby. Atlas Tatr: przyroda nieożywiona. Tatrzański Park Narodowy, Zakopane, Poland.
Skiba, M., Szczerba, M., Skiba, S., Bish, D.L., Grybos, M., 2011. The nature of interlayering in clays from a podzol (Spodosol) from the Tatra Mountains, Poland. Geoderma 160, 425–433. https://doi.org/10.1016/j.geoderma.2010.10.013.
Skiba, S., 1977. Studies on mountain soils formed in various phytoclimatic zones of the crystalline part of the Polish Tatra Mts. Roczniki Gleboznawcze – Soil Science Annual 28(1), 205–241. (in Polish with English abstract).
Skiba, S., 1983. Tendencies towards zonality in the rendzinas of the Tatra Mts. (with the soils of the slope of Mt. Kominiarski Wierch as an example). Roczniki Gleboznawcze – Soil Science Annual 34, 101–112. (in Polish with English abstract).
Skrzydłowski, T., 2013. Przewodnik przyrodniczy po Tatrach Polskich. Wydawnictwo Tatrzańskiego Parku Narodowego, Zakopane, Poland, p. 424.
Soil Science Division Staff, 2017. Soil Survey Manual. Ditzler, C., Scheffe, K., Monger H. C. (Eds.) USDA Handbook 18. Washington, D.C.
Stolarczyk, M., Musielok, Ł., Szymański, W., Drewnik, M., 2024. Morphology, properties and classification of folisols in the Tatra Mountains. Soil Sci. Annu. 75 (4), 195239. https://doi.org/10.37501/soilsa/195239.
Strzemski, M., 1956. Gleby Tatr Polskich. Roczniki Gleboznawcze – Soil Science Annual 5, 3–71. In Polish with English Abstract.
Swęd, M., Uzarowicz, Ł., Duczmal-Czernikiewicz, A., Kwasowski, W., Pędziwiatr, A., Siepak, M., Niedzielski, P., 2022. Forms of metal(loid)s in soils derived from historical calamine mining waste and tailings of the Olkusz Zn–Pb ore district, southern Poland: A combined pedological, geochemical and mineralogical approach. Appl. Geochem. 139, 105218. https://doi.org/10.1016/j.apgeochem.2022.105218.
Tarnawczyk, M., Uzarowicz, Ł., Perkowska-Pióro, K., Pędziwiatr, A., Kwasowski, W., 2021. Effect of land reclamation on soil properties, mineralogy and trace-element distribution and availability: the example of Technosols developed on the tailing disposal site of an abandoned Zn and Pb mine. Minerals 11 (6), 559. https://doi.org/10.3390/min11060559.
Thompson, R., Oldfield, F., 1986. Environmental Magnetism. Allen and Unwin, London. https://doi.org/10.1007/978-94-011-8036-8.
Uzarowicz, Ł., Górka-Kostrubiec, B., Dudzisz, K., Rachwal, M., Zagórski, Z., 2021. Magnetic characterization and iron oxide transformations in Technosols developed from thermal power station ash. Catena 202, 105292. https://doi.org/10.1016/j.catena.2021.105292.
Uzarowicz, Ł., Skiba, S., 2011. Technogenic soils developed on mine spoils containing iron sulphides: Mineral transformations as an indicator of pedogenesis. Geoderma 163, 95–108. https://doi.org/10.1016/j.geoderma.2011.04.008.
Uzarowicz, Ł., Zagórski, Z., Mendak, W., Bartmiński, P., Szara, E., Kondras, M., Oktaba, L., Turek, A., Rogoziński, R., 2017. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. Properties, classification, and indicators of early pedogenesis. Catena 157, 75–89. https://doi.org/10.1016/j.catena.2017.05.010.
Uzarowicz, Ł., Kwasowski, W., Śpiewak, O., Świtoniak, M., 2018a. Indicators of pedogenesis of Technosols developed in an ash settling pond at the Bełchatów thermal power station (central Poland). Soil Sci. Annu. 69 (1), 49–59. https://doi.org/10.2478/ssa-2018-0006.
Uzarowicz, Ł., Skiba, M., Leue, M., Zagórski, Z., Gąsiński, A., Trzciński, J., 2018b. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part II. Mineral Transformations and Soil Evolution. Catena 162, 255–269. https://doi.org/10.1016/j.catena.2017.11.005.
Uzarowicz, Ł., Charzyński, P., Greinert, A., Hulisz, P., Kabała, C., Kusza, G., Kwasowski, W., Pędziwiatr, A., 2020a. Studies of technogenic soils in Poland: past, present, and future perspectives. Soil Sci. Annu. 71, 281–299. https://doi.org/10.37501/soilsa/131615.
Uzarowicz, Ł., Wolińska, A., Błońska, E., Szafranek-Nakonieczna, A., Kuźniar, A., Słodczyk, Z., Kwasowski, W., 2020b. Technogenic soils (Technosols) developed from mine spoils containing Fe sulphides: Microbiological activity as an indicator of soil development following land reclamation. Appl. Soil Ecol. 156, 103699. https://doi.org/10.1016/j.apsoil.2020.103699.
Uzarowicz, Ł., Swęd, M., Kwasowski, W., Pędziwiatr, A., Kaczmarek, D., Koprowska, D., Górka-Kostrubiec, B., Pawłowicz, E., Murach, D., 2024. Initial pedogenic processes, mineral and chemical transformations and mobility of trace elements in Technosols on dumps of the former copper mines in Miedziana Góra and Miedzianka, the Świętokrzyskie Mts., south-central Poland. Catena 245, 108293. https://doi.org/10.1016/j.catena.2024.108293.
Van Reeuwijk, L.P., 2002. Procedures for soil analysis. Technical Paper 9. ISRIC, Wageningen.
Warr, L.N., 2021. IMA–CNMNC approved mineral symbols. Mineral. Mag. 85, 291–320. https://doi.org/10.1180/mgm.2021.43.
Warzyński, H., Sosnowska, A., Harasimiuk, A., 2018. Effect of variable content of organic matter and carbonates on results of determination of granulometric composition by means of Casagrande's areometric method in modification by Prószyński. Soil Sci. Annu. 69 (1), 39–48. https://doi.org/10.2478/ssa-2018-0005.
Wasak, K., 2014. Cellulose decomposition rate and features of organic matter in forest soils in the Tatra Mountains. Fundament. Appl. Soil Sci. 15, 70–80. https://doi.org/10.15421/041407.
Wasak, K., Drewnik, M., 2015. Land use effects on soil organic carbon sequestration in calcareous Leptosols in former pastureland-a case study from the Tatra Mountains (Poland). Solid Earth 6, 1103–1115. https://doi.org/10.5194/se-6-1103-2015.
Wasak, K., Drewnik, M., 2016. Properties of humus horizons of soils developed in the lower montane belt in the Tatra Mountains. Polish J. Soil Sci. 45, 57. https://doi.org/10.17951/PJSS.2012.45.1.57.
Wasak-Sęk, K., 2017. Wpływ materiału macierzystego i roślinności na właściwości materii organicznej gleb regla dolnego w Tatrach Zachodnich. Jagiellonian University in Kraków. PhD Dissertation.
Wątocki, W., 1950. Żyły mineralne na Ornaku w Tatrach Zachodnich. Ann. Soc. Geol. Pol. 20, 11–60.
Wieczorek, J., Zadrożny, P., 2013. Content of Cd, Pb and Zn in podzols Tatra National Park. Proc. ECOpole 7 (1), 57. https://doi.org/10.2429/proc.2013.7(1)057 (in Polish with English abstract).
Wilson, M.J., 2004. Weathering of primary rock-forming minerals: processes, products and rates. Clay Miner. 39, 233–266. https://doi.org/10.1180/0009855043930133.
Woś, B., Pietrzykowski, M., 2020. Characteristics of technogenic soils developed from Neogene and Quaternary sediments substrate on reclaimed sulphur and sand extraction mine sites. Soil Sci. Annu. 71 (4), 344–351. https://doi.org/10.37501/soilsa/126996.
Zamanian, K., Pustovoytov, K., Kuzyakov, Y., 2016. Pedogenic carbonates: Forms and formation processes. Earth Sci. Rev. 157, 1–17. https://doi.org/10.1016/j.earscirev.2016.03.003.
Zwoliński, S., 1960. Z dziejów górnictwa i hutnictwa w Tatrach. Rudy Żelaza. 5, 11–14.

Warsaw, 29.09.2025

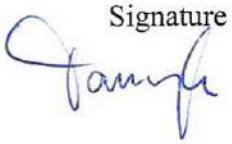
Magdalena Tarnawczyk
mtarnawczyk@gmail.com

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Górka-Kostrubiec B., Pędziwiatr A., 2024. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena, 247, 108521, my individual contribution to its creation consisted of the major part of the work presented in this publication, including conceptualization, methodology, investigation, data curation, writing – original draft, writing – review & editing, validation, visualization, funding acquisition, project administration.

Signature



Warsaw, 29.09.2025

Łukasz Uzarowicz
lukasz_uzarowicz@sggw.edu.pl

Agriculture and Horticulture Discipline Council of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Górka-Kostrubiec B., Pędziwiatr A., 2024. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena, 247, 108521, my individual contribution to its creation consisted of writing – review and editing, writing – original draft, validation, supervision, methodology, investigation, funding acquisition, data curation, conceptualization.

Signature

Warsaw 29.09.2025

Wojciech Kwasowski
Wojciech_kwasowski@sggw.edu.pl

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Górka-Kostrubiec B., Pędziwiatr A., 2024. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena, 247, 108521, my individual contribution to its creation consisted of: Writing – review and editing, Validation, Supervision, Methodology, Investigation, Conceptualization.

Signature

Warsaw, 26.09.2025

Beata Górka-Kostrubiec
kostrub@igf.edu.pl

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Górka-Kostrubiec B., Pędziwiatr A., 2024. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena, 247, 108521, my individual contribution to its creation consisted of investigation, methodology, validation and writing – review & editing.

Signature

Warsaw, 29.09.2025

Artur Pędziwiatr
artur_pedziwiatr@sggw.edu.pl

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Górka-Kostrubiec B., Pędziwiatr A., 2024. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena, 247, 108521, my individual contribution to its creation consisted of writing – review and editing, validation, methodology, investigation, conceptualization.

Signature

Pędziwiatr Artur

SOIL SCIENCE ANNUAL
2025, 76(3), 211370

https://doi.org/10.37501/soilsa/211370

Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland

Magdalena Tarnawczyk[a*], Łukasz Uzarowicz[a], Artur Pędziwiatr[a], Wojciech Kwasowski[a]

[a] Warsaw University of Life Sciences – SGGW, Institute of Agriculture, Department of Soil Science, Nowoursynowska Str. 159, building no. 37, 02-776 Warsaw, Poland

* Corresponding author: Magdalena Tarnawczyk, MSc. Eng., magdalena_tarnawczyk@sggw.edu.pl, ORCID iD: https://orcid.org/0000-0001-7324-0812

Received: 2025-08-09
Accepted: 2025-09-26
Published online: 2025-09-26
Associated editor: Cezary Kabała

Keywords:

Spolic Technosols
Soil-forming processes
Soil micromorphology
Mountain soils
Historical mining
Historical smelting

Abstract

Spolic Technosols developed from mine and metallurgical wastes in areas of historical mining and smelting activities undergo natural weathering, soil-forming and biological processes. This study presents (1) micromorphological and submicromorphological features using optical microscopy and scanning electron microscopy, as well as (2) chemical characteristics based on selective extractions of pedogenic Fe, Al, Mn and Si in Technosols from the Tatra Mountains, southern Poland, to identify key pedogenic processes in these soils. This approach provides insight into the complex pedogenesis of Spolic Technosols in an alpine environment influenced by past industrial activity. Thirteen soil profiles were analysed, divided into three groups: (I) Technosols formed from mine wastes comprising Fe- and Mn-ore-bearing carbonate rocks (limestones and dolomites), (II) Technosols developed from mine wastes derived from polymetallic ore-bearing igneous and metamorphic rocks (granite, gneiss), and (III) Technosols containing wastes from smelting activity (e.g. metallurgical slags). Soil thin section analysis revealed the following microscale evidences of initial soil formation: (1) formation of Fe oxide pseudomorphs due to sulphide weathering; (2) formation of pedogenic structure; (3) formation of pedogenic carbonate coatings in soils developed from mine wastes composed of carbonate rocks; (4) formation of pedogenic Fe and Mn oxide coatings in acidic soils developed from mine wastes composed of crystalline rocks (granite, gneiss); (5) formation of pedogenic sulphate coatings in soils containing metallurgical wastes, and (6) bioturbations (e.g. root channels and biogenic channels filled with a material reworked by soil animals). Micromorphological observations also showed that metallurgical slags in Technosols can serve as a habitat for soil fauna (most likely nematodes or enchytraeids). Selective extractions of pedogenic Fe, Al, Mn, and Si showed (1) the release of oxalate-extractable Mn in soils developed from Mn-bearing ore mine wastes, (2) a slight mobilisation of oxalate-extractable Fe and Al in acidic Technosols developed from aluminosilicate parent material, and (3) the release of oxalate-extractable Al and Si in Technosols containing metallurgical slags. These results indicate that technogenic parent materials undergo weathering, which will most likely consequently transform the mineral composition of the studied Technosols in the future. This study contributes to expanding knowledge of Technosols and their potential ecological functions in mountain regions. It also provides insights into soil development in areas of historical mining and metallurgical activities in an alpine environment of the Tatra Mountains.

1. Introduction

The study of soils in areas affected by historical human activities provides valuable insights into pedogenic processes and the long-term environmental effects of anthropogenic disturbances. Technosols, recognised by the World Reference Base for Soil Resources (IUSS Working Group WRB, 2022), are characterised by the presence of artefacts that are human-made, human-altered, and human-excavated materials (Charzyński et al., 2013; Uzarowicz et al., 2020a). Important soils among them are Spolic Technosols, which develop, for example, at disposal sites containing mine and industrial wastes (Néel et al.,

2003; Kabała et al., 2020; Swęd et al., 2022). These soils are commonly found in contemporary industrial areas (Grünewald et al., 2007; Uzarowicz et al., 2017; Allory et al., 2022). However, they also occur in places of historical industrial activity, which nowadays are often covered with vegetation due to natural plant succession (Woś et al., 2023; Castillo Corzo et al., 2025; Uzarowicz et al., 2025). Sometimes, these areas can comprise ecologically sensitive environments and protected areas. An example of such a site is the Tatra Mountains, currently protected as the Tatra National Park.

The Tatra Mountains, part of the Western Carpathians, are a high mountain area in southern Poland and northern Slovakia with a long history of mining and metallurgical activity (Jost, 2004; Rączkowska, 2019). Mining and metallurgy in the Tatra Mountains lasted from the 15th century until the end of the 19th century (Radwańska-Paryska and Paryski, 1995), with the greatest environmental impact in the 18th and early 19th centuries (Zwoliński, 1984). Mining and metallurgy activities have left a legacy of altered landscapes as well as mine wastes and metallurgical slags deposited on the land surface, affecting biodiversity and soil quality (Mirek, 1996). These anthropogenic materials are unique soil substrates from which Spolic Technosols develop after covering a post-industrial area with vegetation. Although the properties and geochemical features of Technosols in historical metal mining and smelting areas in the Tatra Mountains were recently identified and described (Tarnawczyk et al., 2024, 2025), the advancement of soil-forming processes in these soils is still poorly recognised. Therefore, there is a need to extend our knowledge about soil development in abandoned mining and smelting areas. This combined micromorphological and chemical approach provides novel insights into soil-forming processes in high-mountain Technosols, which have not been studied in detail in the Tatra Mountains before.

Micromorphological analysis, which aims to recognise soil characteristics at the micro-scale, in addition to chemical analyses on pedogenic forms of Fe, Al, Mn, and Si, offers a valuable tool for studying the effects of early soil-forming processes in Technosols. In the last two decades, soil micromorphology has become more and more frequently used to study the genesis of Technosols (Zikeli et al., 2002; Zanuzzi et al., 2009; Séré et al., 2010; Uzarowicz and Skiba, 2011; Jangorzo et al., 2013; Huot et al., 2015; Uzarowicz et al., 2017, 2018b; Watteau et al., 2017; Ortega et al., 2022). Recent micromorphological studies (e.g., Huot et al., 2014b; Watteau et al., 2018, 2025; Colombini et al., 2020; Ruiz et al., 2022; Díaz-Ortega et al., 2024) have focused on the investigation of pedogenic processes in human-affected soils of industrial regions in lowland and upland areas. However, comparable data from high mountain environments are scarce. Identifying micromorphological features of the groundmass, soil organic matter, and pedofeatures reveals the interplay between anthropogenic influences and natural soil-forming processes (Zaiets and Poch, 2016; Stoops et al., 2018; Verrecchia and Trombino, 2021). Previous studies on soil micromorphology in the Tatra Mountains, such as those by Zasoński and Niemyska-Łukaszuk (1977), Miechówka and Ciarkowska (1998), and Drewnik (2008), have primarily focused on the determination of properties of natural (non-anthropogenic) soils; however, soils in the areas affected by historical mining and smelting activities have not been investigated.

Selective extractions of Fe, Al, Si, and Mn from soils are frequently used to differentiate mineralogical and chemical forms of Fe, Al, Si, and Mn in soils, as well as to assess pedogenic transformations and mineral weathering, which is helpful in identifying the degree of advancement of soil-forming processes and in distinguishing between different soil types (McKeague and Day, 1966; Cornell and Schwertmann, 2003). Selective extractions of Fe, Al, Si, and Mn for Technosols developed from different anthropogenic parent materials (thermal power station ash, mine wastes containing Fe and Cu sulphides; mine wastes from sedimentary Fe ore mines) indicate the release of these elements in soil environment and proves that the results of the extractions can be a good indicator of initial soil-forming processes in Technosols (Uzarowicz and Skiba, 2011; Uzarowicz et al., 2017, 2024, 2025). It seems that the selective extractions of Fe, Al, Si, and Mn should also be used for Technosols developed from other anthropogenic parent materials, including technogenic soils of the Tatra Mountains.

The purpose of this study was to determine the degree of advancement of soil-forming processes in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains (southern Poland), based on micromorphological, submicromorphological, and chemical indicators of pedogenesis. We hypothesised that (1) micromorphological and submicromorphological features, together with pedogenic forms of Fe, Al, Si, and Mn, can be used to trace the intensity and direction of soil-forming processes over several centuries of Technosol development, and (2) these features provide insights into the genesis of high-mountain Technosols and their ecological implications in human-influenced mountain ecosystems.

2. Materials and methods

2.1. Study area

The study was conducted in the Tatra Mountains, the highest range of the Carpathians, located in southern Poland along the border with Slovakia. This region is characterised by an alpine environment, with elevations ranging from approximately 900 to 2500 meters above sea level. The climatic conditions are harsh, with the mean annual air temperatures ranging from 6°C in the valleys to –4°C near the peaks, and the mean annual precipitation from 1000 mm in the lowest part up to 1800 mm in the highest part of the mountains (Hess, 1996).

The Tatra Mountains are part of the Western Carpathians and consist predominantly of granitoids in the High Tatras and metamorphic rocks in the Western Tatras, as well as sedimentary rocks in the lower part of the Western Tatras (Kotański, 1971; Passendorfer, 1996; Gradziński et al., 2001). The relief of the Tatra Mountains is shaped by glacial, fluvial, and slope processes, creating a complex landscape of valleys and ridges (Klimaszewski, 1996).

The Tatra Mountains are a typical alpine environment with distinct altitudinal vegetation zones. The lowest zone, up to about 1250 m a.s.l., is dominated by beech (*Fagus sylvatica* L.) and fir (*Abies alba* Mill.), while spruce (*Picea abies* (L.) H. Karst) is also widespread due to past forest management. Between 1250 and 1550 m a.s.l., the upper forest belt develops, dominated by spruce and silver birch (*Betula pendula* Roth). Above, in the subalpine zone (1550–1800 m a.s.l.), the main component of the vegetation is dwarf pine (*Pinus mugo* Turra) scrub. At an altitude of 1800–2300 m a.s.l., alpine grasslands predominate, with species such as *Juncus trifidus* and *Festuca varia*, while above 2300 m a.s.l., the subnival zone is characterised by lichens, mosses, and low grasses in harsh climatic conditions (Piękoś-Mirkowa and Mirek, 1996).

The mosaic pattern is very characteristic of the soil cover in the Tatra Mountains (Komornicki and Skiba, 1996). The soils have diverse properties depending mostly on parent rock (various igneous, sedimentary, and metamorphic rocks), vegetation, morphogenetic processes, and climatic conditions (Komornicki and Skiba, 1996). The most common soils occurring in the Tatra Mountains are Podzols, rendzina soils (Rendzic Leptosols), brown soils (Cambisols), as well as initial soils (Leptosols and Regosols) (Komornicki and Skiba, 1996; Drewnik et al., 2008).

Historical mining and metallurgical activities, conducted particularly from the medieval period to the end of the 19th century, have locally influenced the region's soil substrates (Osika, 1987; Jost, 2004). The remnants of these activities are, for example, mine waste heaps and slag disposal sites, which serve as parent materials for Spolic Technosols investigated in the present study.

2.2. Study object

The study focuses on Spolic Technosols developed in areas of historical mining and metallurgy in the Tatra Mountains. These soils were formed from anthropogenic substrates including mine waste and metallurgical slags originating from the extraction and processing of copper (Cu), iron (Fe), silver (Ag), manganese (Mn), and antimony (Sb) ores (Wątocki, 1950; Jost, 1962, 2004). In the Polish part of the Tatra Mountains, mining activity developed mainly in the Western Tatras (the Chochołowska and Kościeliska Valley region, including the Ornak ridge), whereas the metallurgical centres were located in Kuźnice and the Kościeliska Valley (Liberak, 1927).

Thirteen soil profiles from eight selected sites located on small heaps at adit outlets, near collapsed adits and shafts, and in historical smelting areas were examined. Detailed location of the soil profiles, including a map and images of representative profiles with surrounding vegetation, was presented elsewhere (Tarnawczyk et al., 2024). The profiles were located at the following sites: (a) the Huciańskie Banie (profiles 1 and 2); (b) mouth of the Kościeliska Valley (profile 3); (c) the Kościeliska Valley near the Ornak tourist shelter (profile 4); (d) the Pyszniańska Valley (profiles 5 and 6); (e) the Żleb pod Banie (Pod Banie Couloir) at the Ornak ridge (profiles 7 and 8); (f) the Banisty Żleb (Banisty Couloir) at the Ornak ridge (profiles 9 and 10); (g) the Kościeliska Valley – old steelwork at Stare Kościeliska (profiles 11 and 12); and (h) Kuźnice steelwork area (profile 13). The periods of activity of the studied mining and smelting sites are listed in Tarnawczyk et al. (2024). These sites reflect the variability in parent material petrology, mineral composition, soil properties, and differences in vegetation cover. Soil samples were taken from each horizon distinguished in the soil profiles.

The studied soils were classified as different variants of Spolic Technosols or Coarsic Spolic Technosols (Tarnawczyk et al., 2024) (Table 1), following the guidelines of the World Reference Base for Soil Resources (IUSS Working Group WRB, 2022). These soils were grouped based on their properties and the character of parent materials (Tarnawczyk et al., 2024). Group I includes Technosols formed from mine wastes comprising Fe- and Mn-ore-bearing carbonate rocks (limestones and dolomites), represented by profiles 1–3. Group II comprises Technosols developed from mine wastes derived from polymetallic ore-bearing igneous and metamorphic rocks (granite, gneiss), represented by profiles 5–10. Group III includes Technosols containing metallurgical wastes (e.g., slags), represented by profiles 11–13. Profile 4 combines the properties of group I and II. The age of soils was estimated based on information about the time of the operation of a mine or smelter at each study site (Jost, 2004) (Table 1). We suppose that the soils began to develop after the deposition of mine or metallurgical wastes on the land surface.

2.3. Laboratory analyses

2.3.1. Soil properties

The basic physicochemical properties of the studied Technosols were determined in accordance with standard pedological procedures (Van Reeuwijk, 2002; Pansu and Gautheyrou, 2006; Soil Science Division Staff, 2017). Soil samples from each horizon were air-dried, sieved to a size of <2 mm, and analysed for particle size distribution (Bouyoucos–Casagrande method, modified by Prószyński) (Warzyński et al., 2018), pH (potentiometric, H_2O, 1:2.5), carbonate content (Scheibler volumetric method), total organic carbon (TOC), total nitrogen (TN), and total sulphur (TS) using a CHNS elemental analyser (vario MACRO cube, Elementar). In carbonate-containing samples, inorganic C was subtracted from TOC. The mass-specific magnetic susceptibility (χ) was measured with a multifunction MFK1-FA Kappabridge, following Thompson and Oldfield (1986). A full description of the methodology and results is provided in Tarnawczyk et al. (2024). These parameters provide an essential background for the micromorphological study.

2.3.2. Micromorphological analyses

The undisturbed samples were collected from the selected soil horizons. The samples were then air-dried and impregnated with Araldite 2020 epoxy resin. Polished thin sections with a thickness of 30 μm were prepared from the impregnated soil materials at the Faculty of Geology, University of Warsaw, Poland. They were examined in transmitted light using petrographic microscopes (Olympus SZX Z10, Olympus BX41). The micromorphological description and terminology given by Stoops (2021) were applied.

Table 1
Selected physical and chemical properties of the studied soils based on Tarnawczyk et al. (2024)

Horizon	Depth (cm)	Munsell colour (moist)*	Rock fragments (%)*	Percentage of fractions (mm)			Soil textural class (USDA)	Magnetic susceptibility (χ) ($\times 10^{-8} \cdot m^3 \cdot kg^{-1}$)	pH_{H2O}	eq. $CaCO_3$ (%)	TOC (%)	TN (%)	TS (%)
				2.0–0.05	0.05–0.002	< 0.002							
Profile 1 – *Spolic Technosol (Loamic, Eutric, Calcaric, Humic, Hyperartefactic, Skeletic, Toxic)* Approximate time of soil origin: late 18th c. – mid-19th c.													
Oi	0–1	10YR 2/2	–	–	–	–	–	–	–	–	42.40	1.46	0.10
AC1	1–5	10YR 3/1	15	76	17	7	SL	83.5	7.4	20.5	8.19	0.56	0.08
AC2	5–15	10YR 3/2	60	76	15	9	SL	91.4	7.9	31.2	2.18	0.12	0.04
C	15–35	2.5YR 3/3	70	75	15	10	SL	36.8	8.0	30.4	1.85	0.07	0.04
2C	35–60	10YR 2/2	80	54	30	16	SL	12.5	8.1	21.5	1.06	0.11	0.02
Profile 2 – *Spolic Technosol (Loamic, Eutric, Calcaric, Humic, Hyperartefactic, Skeletic, Toxic)* Approximate time of soil origin: late 18th c. – mid-19th c.													
Oi	0–1	–	–	–	–	–	–	–	–	–	43.97	0.98	0.07
AC1	1–25	10YR 2/2	40	75	19	6	SL	32.2	7.5	22.1	6.62	0.44	0.06
AC2	25–45	10YR 3/1	60	70	21	9	SL	33.7	7.9	21.2	2.63	0.17	0.03
AC3	45–65	10YR 3/2	70	65	23	12	SL	32.6	7.9	20.8	2.42	0.15	0.04
2C	65–90	2.5YR 3/2	80	46	40	14	L	22.4	7.8	9.6	2.70	0.24	0.04
Profile 3 – *Spolic Technosol (Epiarenic, Endoloamic, Eutric, Dolomitic, Mollic, Hyperartefactic, Skeletic)* Approximate time of soil origin: late 18th c. – 19th c.													
Oe	0–6	7.5YR 3/3	–	–	–	–	–	–	5.7	–	41.22	1.65	0.13
O/C	6–25	10YR 2/1	70	87	9	4	LS	32.3	6.8	11.1	23.57	1.11	0.12
AC	25–40	10YR 2/2	70	81	15	4	LS	15.1	7.2	17.0	10.69	0.53	0.07
BC	40–60	10YR 3/4	40	70	24	6	SL	6.5	7.6	26.5	5.14	0.26	0.04
Profile 4 – *Spolic Technosol (Epiarenic, Endoloamic, Eutric, Humic, Hyperartefactic)* Approximate time of soil origin: late 18th c. – early 19th c.													
Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
A	1–13	10YR 2/2	50	85	11	4	LS	22.3	6.1	n	8.41	0.54	0.06
C1	13–35	7.5YR 5/4	30	58	25	17	SL	8.0	6.8	n	0.49	0.07	0.02
C2	35–60	10YR 5/4	30	57	25	18	SL	7.9	6.9	n	0.29	0.06	0.01
Profile 5 – *Spolic Technosol (Arenic, Epidystric, Endoeutric, Protocambic, Humic, Hyperartefactic, Skeletic, Toxic)* Approximate time of soil origin: 15th c. – late 19th c.													
Oe	0–3	10YR 2/2	–	–	–	–	–	–	4.1	–	44.95	2.06	0.15
Oa	3–10	10YR 2/1	–	–	–	–	–	–	3.7	–	23.09	1.20	0.12
A	10–15	10YR 2/1	50	86	11	3	LS	15.6	4.0	n	4.62	0.29	0.10
Bw	15–20	10YR 3/3	70	78	18	4	LS	13.4	4.4	n	1.79	0.14	0.09
C	20–45	10YR 4/2	90	77	19	4	LS	14.0	6.0	n	1.01	0.09	0.08
Profile 6 – *Spolic Technosol (Epiloamic, Endoarenic, Dystric, Protocambic, Humic, Hyperartefactic, Skeletic, Toxic)* Approximate time of soil origin: 15th c. – late 19th c.													
Oe	0–2	10YR 2/2	–	0	0	0	–	–	4.0	–	37.86	1.67	0.14
Oa	2–10	10YR 2/1	–	0	0	0	–	–	3.6	–	27.23	1.23	0.11
ABw	10–20	10YR 3/3, 4/3	50	76	16	8	SL	10.2	3.9	n	1.16	0.10	0.06
C	20–65	5YR 5/1	90	79	14	7	LS	10.8	5.5	n	0.63	0.07	0.16

Table 1 – continue

Horizon	Depth (cm)	Munsell colour (moist)*	Rock fragments (%)*	Percentage of fractions (mm)			Soil textural class (USDA)	Magnetic susceptibility (χ) ($\times 10^{-8} \cdot m^3 \cdot kg^{-1}$)	pH_{H2O}	eq. $CaCO_3$ (%)	TOC (%)	TN (%)	TS (%)
				2.0–0.05	0.05–0.002	< 0.002							
Profile 7 – *Spolic Technosol (Epiarenic, Endoloamic, Dystric, Humic, Hyperartefactic, Skeletic)* Approximate time of soil origin: 15th c. – late 19th c.													
Oe	0–2	–	–	–	–	–	–	–	3.7	–	40.47	1.54	0.13
AC	2–15	10YR 2/1	50	86	13	1	S	32.5	3.8	n	10.93	0.65	0.08
C	15–50	10YR 3/4	70	65	32	3	SL	15.3	4.6	n	1.96	0.15	0.02
Profile 8 – *Spolic Technosol (Arenic, Dystric, Humic, Hyperartefactic, Skeletic, Toxic)* Approximate time of soil origin: 15th c. – late 19th c.													
Oe	0–4	–	–	–	–	–	–	–	4.0	–	46.96	1.58	0.12
AC	4–15	10YR 2/2	40	81	18	1	LS	15.5	3.8	n	3.02	0.16	0.57
C1	15–35	10YR 2/2	70	81	16	3	LS	11.8	4.5	n	1.26	0.10	0.15
C2	35–55	10YR 3/4	80	79	18	3	LS	10.5	4.3	n	1.44	0.11	0.12
Profile 9 – *Coarsic Spolic Technosol (Arenic, Amphiloamic, Dystric, Ochric, Hyperartefactic, Skeletic, Toxic)* Approximate time of soil origin: 16th c. – 19th c.													
Oi	0–2	–	–	–	–	–	–	–	–	–	45.82	0.91	0.08
AC	2–10	10YR 3/2	80	79	15	6	LS	14.4	4.4	n	1.05	0.10	0.40
C1	10–40	10YR 4/2	90	76	16	8	SL	14.4	4.5	n	0.88	0.09	0.37
C2	40–80	10YR 4/2	90	79	15	6	LS	13.3	4.5	n	0.86	0.09	0.53
Profile 10 – *Coarsic Spolic Technosol (Loamic, Dystric, Humic, Hyperartefactic, Skeletic, Toxic)* Approximate time of soil origin: 16th c. – 19th c.													
Oi	0–1	–	–	–	–	–	–	–	–	–	47.90	0.90	0.07
AC	1–10	10YR 3/2	70	76	17	7	SL	39.0	4.4	n	1.48	0.10	0.07
C1	10–50	10YR 4/2	90	77	16	7	SL	14.8	4.4	n	1.16	0.09	0.07
C2	50–70	10YR 4/4	70	76	18	6	SL	15.2	4.5	n	1.42	0.12	0.06
Profile 11 – *Spolic Technosol (Epiarenic, Endoloamic, Eutric, Carbonic, Humic, Hyperartefactic, Pyric, Toxic)* Approximate time of soil origin: 18th c. – early 19th c.													
Oi	0–1	–	–	–	–	–	–	–	–	–	40.20	1.22	0.09
A	1–15	10YR 2/1	5	79	14	7	LS	3313.6	5.6	n	9.13	0.55	0.06
C1	15–30	10YR 2/2, 4/3	10	65	26	9	SL	3342.2	6.0	n	5.24	0.29	0.04
C2	30–45	10YR 2/1	15	67	27	6	SL	7064.4	6.2	n	8.84	0.28	0.04
C3	45–60	10YR 2/1	20	69	26	5	SL	10485.6	6.5	n	10.60	0.22	0.04
Profile 12 – *Spolic Technosol (Epiarenic, Endoloamic, Eutric, Carbonic, Humic, Hyperartefactic, Pyric, Toxic)* Approximate time of soil origin: 18th c. – early 19th c.													
Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
A	1–20	10YR 2/1	20	76	19	5	LS	4683.8	5.8	n	8.04	0.42	0.05
C1	20–28	10YR 5/4	20	67	24	9	SL	489.4	6.1	n	2.55	0.21	0.10
2C	28–50	10YR 2/1	50	65	29	6	SL	9480.3	6.1	n	14.69	0.16	0.03
3C	50–60	5YR 4/4	40	70	23	7	SL	161.2	6.6	1.7	1.44	0.08	0.75
4C	60–75	10YR 4/3	30	61	29	10	SL	36.6	6.4	n	1.87	0.18	0.05
Profile 13 – *Spolic Technosol (Arenic, Eutric, Humic, Hyperartefactic, Relocatic, Skeletic)* Approximate time of soil origin: late 18th c. – late 19th c.													
Oi	0–1	–	–	–	–	–	–	–	–	–	45.07	1.18	0.07
AC	1–15	10YR 2/1	80	80	18	2	LS	128.0	7.0	1.3	6.03	0.38	0.10
2C	15–25	10YR 5/3	50	84	11	5	LS	28.3	8.6	5.8	5.63	0.38	0.10

Explanations: – not analysed; n – not detected; * measured during field works; L – loam; LS – loamy sand; S – sand; SL – sandy loam; TOC – total organic carbon; TN – total nitrogen; TS – total sulphur.

2.3.3. SEM-EDS analyses

The selected soil thin sections were studied using a scanning electron microscope equipped with an energy dispersive X-ray spectrometer (SEM-EDS). The samples were carbon-coated before the analyses in SEM-EDS. The SIGMA (Zeiss) field emission SEM was used. The microscope was equipped with the backscattered electron (BSE) detector. The studies were performed in a high vacuum mode using an accelerating voltage of 20 kV. The analyses were performed at the Laboratory of Electron Microscopy, Microanalysis, and X-Ray Diffraction, Faculty of Geology, University of Warsaw, Poland.

2.3.4. Pedogenic forms of Fe, Al, Si, and Mn

The selective extractions of pedogenic Fe, Al, Si, and Mn forms were performed on soil fine earth (<2 mm). The analyses included the following extractions:

- dithionite–citrate–bicarbonate (DCB) Fe extraction; it was used to extract free iron oxides (denoted hereafter as Fe_d), following the procedure by Mehra and Jackson (1958),
- ammonium oxalate extraction using a solution of 0.175 M ammonium oxalate and 0.1 M oxalic acid (at pH 3.0) in the darkness; it was applied to extract amorphous and poorly crystalline forms of Fe, Al, Si, and Mn (denoted hereafter as Fe_{ox}, Al_{ox}, Si_{ox}, and Mn_{ox}), according to the method by Schwertmann (1964).

The Fe, Al, Si, and Mn concentrations in the soil extracts were measured using inductively coupled plasma – optical emission spectrometry (ICP–OES, Perkin Elmer Avio 200). The total iron content (Fe_t) was determined on powdered soil fine earth by total microwave mineralisation (Milestone Ethos UP) in a mixture of concentrated acids (2 ml HNO_3 + 5 ml HF + 2 ml HCl + 1 ml $HClO_4$) and analysis of extracts using ICP-OES. All analyses were performed in duplicates.

Based on the measured forms (Fe_t, Fe_d, Fe_{ox}, Al_{ox}), the following parameters were calculated:

- Fe_{nf} – iron content in forms other than free oxides, calculated as $Fe_{nf} = Fe_t - Fe_d$
- Fe_c – crystalline pedogenic iron oxides, calculated as $Fe_c = Fe_d - Fe_{ox}$
- Fe_d/Fe_t – Fe oxide mobility index
- Fe_{ox}/Fe_d – Fe oxide activity index
- Al_{ox} + ½Fe_{ox} (expressed in %), which is used as one of the indicators of the spodic horizon according to the WRB soil classification system (IUSS Working Group WRB, 2022).

3. Results

3.1. Morphology, properties, and mineral composition of the studied Technosols

Detailed information about properties, mineral and chemical composition, as well as photographs of soil profiles and the surrounding vegetation, was presented elsewhere (Tarnawczyk et al., 2024, 2025). Selected physical and chemical properties are presented in Table 1. Profiles 1–10 represented soils developed from mine waste dumps containing diverse parent materials including limestone and dolomite debris, granite and gneiss fragments. Most profiles showed a simple soil morphology consisting of O, A (or AC) and C horizons, except for profiles 5 and 6, which had Bw horizons suggesting more advanced soil-forming processes. A high content of rock fragments was a common feature of most of the studied profiles. Profiles 11–13 represented Technosols formed in areas of old metallurgical activity. Profiles 11 and 12, near the Stare Kościeliska steelworks, contained slag, ferruginous rocks, charcoals, and building debris. Profile 12 displayed clear layering and contained layers rich in both metallurgical wastes (A and 2C horizons) and mine wastes (3C horizon). Profile 13, at an artificial slag disposal site in Kuźnice, was composed of carbonate-bearing sandy material covered with slag fragments, forming a thin, bipartite soil profile.

Technosols developed from carbonate-rich mine wastes (group I) were characterised by neutral to alkaline reaction (pH from 7.2 to 8.1, except for horizon Oe and O/C in P3 with pH 5.7 and 6.8, respectively), resulting from the high carbonate content (9.6–31.2% $CaCO_3$ eq.) (Table 1) (Tarnawczyk et al., 2024). They exhibited moderate to high concentrations of total organic carbon (TOC) in organic horizons (43% on average; 24% in horizon O/C, P3), with lower values in the mineral horizons (4% on average). These soils contained a high proportion of rock fragments (up to 80%), and the soil texture of the fine earth was sandy loam, loamy sand, or loam. Magnetic susceptibility values varied from 7 to 91 $\times 10^{-8} \cdot m^3 \cdot kg^{-1}$. Mineral composition, as previously determined by X-ray diffraction (XRD) (Tarnawczyk et al., 2024) included calcite, quartz, dolomite, feldspars, hematite, and clay minerals.

Technosols developed from non-carbonate aluminosilicate mine wastes (group II) were acidic (pH 3.8–6.0 in mineral horizons; pH 3.9 in organic horizons, on average) (Table 1) due to the absence of carbonates and the weathering of igneous and metamorphic rocks such as granite and gneiss under a coniferous forest vegetation (Tarnawczyk et al., 2024). The TOC contents were generally lower than in group I (2% on average), with higher values obtained in organic (O) horizons (39% on average). The content of rock fragments often exceeded 70% and the soil texture of the fine earth was dominantly loamy sand. Magnetic susceptibility values were from 10 to 39 $\times 10^{-8} \cdot m^3 \cdot kg^{-1}$. Common minerals included quartz, feldspars, and micas, with occasional presence of jarosite and pyrite.

Technosols containing metallurgical wastes (group III) showed variable reaction from slightly acidic to strongly alkaline (pH from 5.6 to 8.6) (Table 1) (Tarnawczyk et al., 2024). The TOC concentrations were notably higher than in the mining non-carbonate waste soils (7% on average in mineral horizons, 43% on average in organic horizons), with high TOC concentrations in horizons enriched in charcoal (up to 15% horizon 2C in P12). Magnetic susceptibility was exceptionally high (up to 10486 $\times 10^{-8} \cdot m^3 \cdot kg^{-1}$) reflecting the presence of magnetic minerals such as magnetite and wüstite. These soils also contained fayalite, goethite, as well as alumino-silicate and ferrous slag residues.

3.2. Soil micromorphological features

3.2.1. Technosols developed from mine wastes containing carbonate-bearing rocks (group I)

Technosols of group I (profiles 1–3) were composed of carbonate sedimentary rock (limestones, dolomites) fragments with

admixture of siliceous sedimentary rocks and fine soil material occurring between rock fragments (Fig. 1A–F, Table 2). Soil material was characterised by a highly separated complex (intergrain micro-aggregate) microstructure with complex, compound, and simple packing voids, as it was found, e.g., in profile 2, AC1 horizon and profile 1, the transition between C and 2C horizons (Fig. 1 C–F).

The groundmass occurred as crumbs or subangular blocky aggregates with porphyric c/f related distribution (Fig. 1A and B; Table 2). Fragments of carbonate, Fe-bearing, and siliceous rocks, as well as separate carbonate, quartz, and feldspar grains, represented coarse fragments in the aggregates. Iron oxide pseudomorphs after sulphides were identified in the transition between C and 2C horizons in profile 1 (Fig. 1E and F; Fig. 2A). Micromass of topsoil horizons was a dark brown or dark grey material with an undifferentiated b-fabric. Micromass of subsoil horizons was a red or red-brown material with an undifferentiated b-fabric. Roots were occasionally found throughout the soil thin sections.

Few pedofeatures were observed under the optical microscope. Occasional carbonate coatings on ped faces and void walls were found, e.g. in the transition between C and 2C horizons in profile 1 (Fig. 1G and H). These coatings exhibited low birefringence and appeared limpid under crossed polarisers.

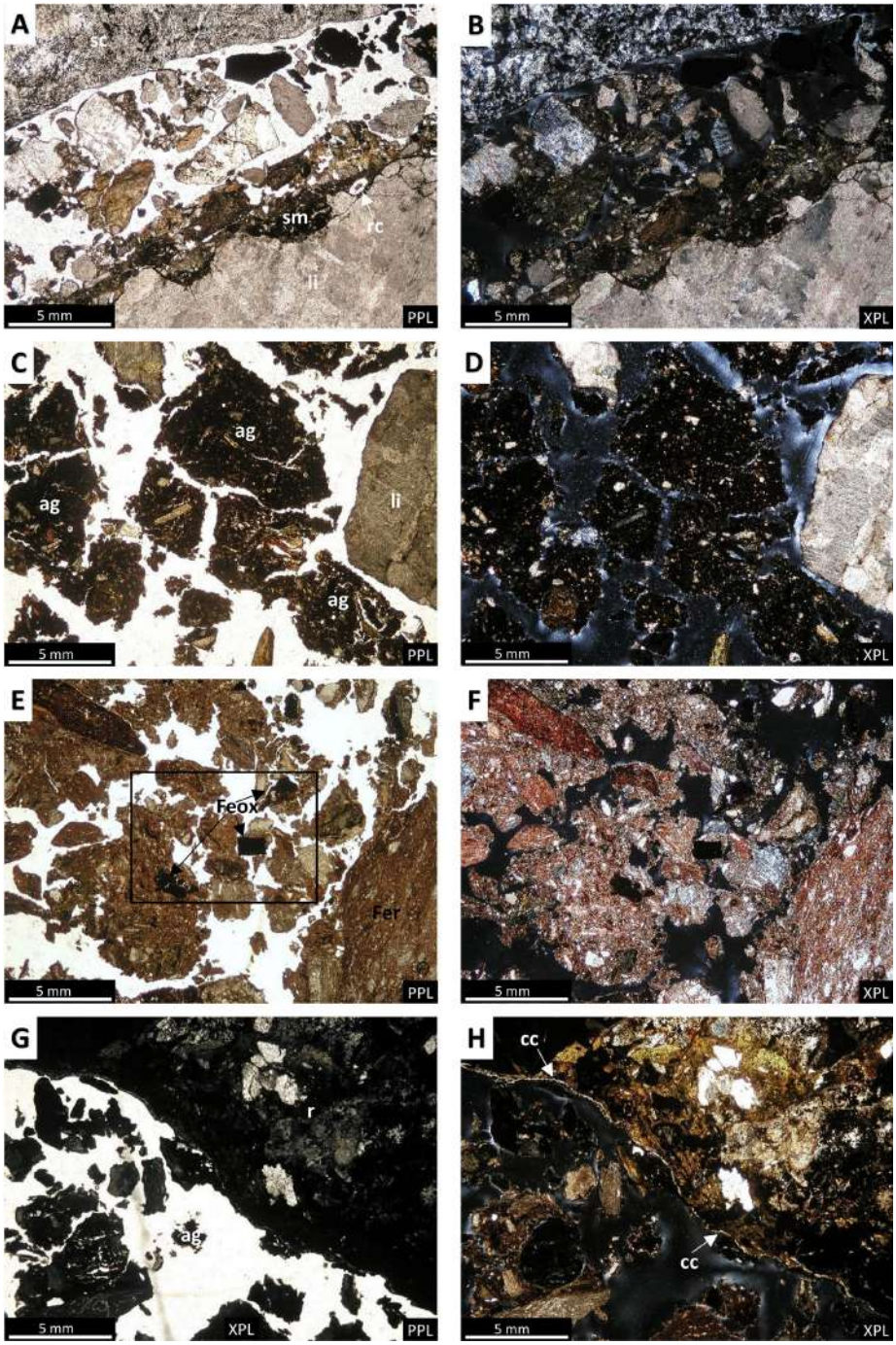


Fig. 1. Micromorphological features of Technosols developed from mine wastes comprising carbonate rocks (group I). **A and B** – profile 1, AC2 horizon. A channel between a limestone (li) and a siliceous rock (sc) filled with rock and mineral fragments. Dark brown soil micromass (sm) rich in humus occurs on a limestone fragment. Root channel (rc) occurs in the micromass. **C and D** – profile 2, AC1 horizon. Limestones (li) and soil aggregates (ag) composed of humic substances and coarse components, including carbonate grains and ferruginous rocks. **E and F** – profile 1, the transition between C and 2C horizons. A groundmass composed of Fe-bearing rocks (Fer), limestone fragments, Fe oxide (Feox) fragments, and a micromass containing clay minerals and dispersed Fe oxides (most likely hematite). A fragment in the framework is shown in detail in Fig. 2A. **G and H** – profile 1, the transition between C and 2C horizons. A carbonate coating (cc) along the pore surrounded by soil aggregates (ag) and a complex sedimentary rock fragment (r) composed, among others, of carbonates and Fe- and Mn-bearing ore minerals. Explanations: PPL – plane-polarized light, XPL – crossed polarizers

Table 2
Micromorphological features of Technosols based on thin sections from selected soil horizons

Profile	Horizon	Depth (cm)	Microstructure	Voids	Rock fragments	Groundmass			Organic matter	Pedofeatures	Other features
						The c/f related distribution	Coarse mineral material	Micromass (fine material): shape, colour, b-fabric			
P1	AC2	5–15	C	SPV	CSR, SiR, FeR	P	C, Qz, Feox, Mnox, Fsp	RBr, G, un	COR, PR	–	PS, MD
P1	transition between C and 2C	~35	C (G, IMA)	SPV, CPV	CSR, SiR, FeR	P	C, Qz, Feox, Mnox, Fsp, Mca	SAB, R, RBr, G, un	C, COR	SCCC	PS, SOM
P2	AC1	1–25	IMA	CXV	CSR, SiR, FeR	P	C, Qz, Feox, Mnox, Fsp, Mca	CA, SAB, RBr, G, un	PR, Ch	–	AS, MV, PS
P4	C1	13–35	S	CXV, PV	IR, MR	–	C, Qz, Fsp, Mca	YRBr, G, un	PR	–	–
P5	transition between A and Bw	~15	SG	SPV	IR, MR	coarse M	Qz, Feox, Fsp, Mca, Chl	RBr, YRBr, un	–	ICC	PS
P6	ABw	10–20	SG	SPV	IR, MR	coarse M	Qz, Feox, Fsp, Mca	RBr, YRBr, un, grs	PR	ICC	PS
P8	transition between AC and C1	~15	C	CXV	IR, MR	–	Qz, Feox, Fsp, Mca, Chl, Brt	G, YBr, un	–	MnC	–
P8	transition between AC and C1	~15	C	CXV	IR, MR	–	Qz, Feox, Fsp, Mca, Chl	G, YBr, un	–	–	BP, AS, WRM
P9	AC	2–10	SG	SPV	IR, MR	–	Qz, Feox, Fsp, Mca	RBr, YRBr, un	PR	ICC	PS, AS
P10	AC and C1	~10	C	CXV	IR, MR	–	Qz, Feox, Fsp, Mca	YBr, G, un	–	–	–
P10	C2	50–70	C	CXV	IR, MR	–	Qz, Feox, Fsp, Mca	YBr, G, un	–	–	–
P11	transition between A and C1	~10	C	CXV	SL, NSR	–	Qz, Feox, Fsp, Mca	CA, Bl, un	Ch	ICC	SO
P11	C2	30–45	C	CXV	SL, NSR	–	Qz, Feox, Fsp, Mca	CA, Bl, un	Ch	ICC	–
P12	A	1–20	C	CXV	SL, NSR	–	Qz, Feox, Fsp, Mca	CA, Bl, un	Ch	ICC	–
P12	2C	28–50	C	CXV	SL, NSR	–	Qz, Feox, Fsp, Mca	CA, Bl, un	Ch	ICC around charcoal	–
P13	AC	1–15	C	CXV	SL	–	Qz	Br, un	–	–	–

Explanations:
– not determined
Microstructure: C – complex microstructure, G – granular microstructure, IMA – intergrain micro-aggregate microstructure, S – subangular blocky microstructure, SG – single grain microstructure
Voids: CPV - compound packing voids, CXV – complex packing voids, PV – planar voids, SPV – simple packing voids
Rock fragments: CSR – carbonate sedimentary rocks (limestones, dolomites), IR – igneous rocks (granite), MR – metamorphic rocks (gneiss), NSR – non-carbonate sedimentary rocks (sandstones, mudstones), SiR – siliceous sedimentary rocks, FeR – Fe-bearing rocks, SL – slags
The c/f related distribution: E – enaulic, M – monic, P – porphyric
Coarse mineral material: Brt – barite, C – carbonates, Chl – chlorite, Fsp – feldspar, Feox – iron oxides, Mnox – manganese oxides, Mca – mica, Qz – quartz
Micromass (fine material): Bl – black, Br – brown, CA – crumb aggregates, G – grey, grs – granostriated b-fabric, R – red, RBr – reddish-brown, SAB – sub-angular blocks, un – undifferentiated b-fabric, YBr – yellowish brown, YRBr – yellowish reddish-brown
Organic matter: Ch – charcoal, COR – carbonate organic remains (in rocks), PR – plant residues
Pedofeatures: BP – biotic pedoturbations (chanells), ICC – Fe oxide coatings, SCCC – secondary Ca carbonates coating, MnC – Mn oxide coatings
Other features: MV – Mn oxide veins (in rocks), MD – Mn oxide dendrites, PS – Fe oxide pseudomorphs after sulphides, SOM – soil organic matter, AS – aggregate structure, WRM – strongly weathered rocks and mineral fragments, SO – soil organisms

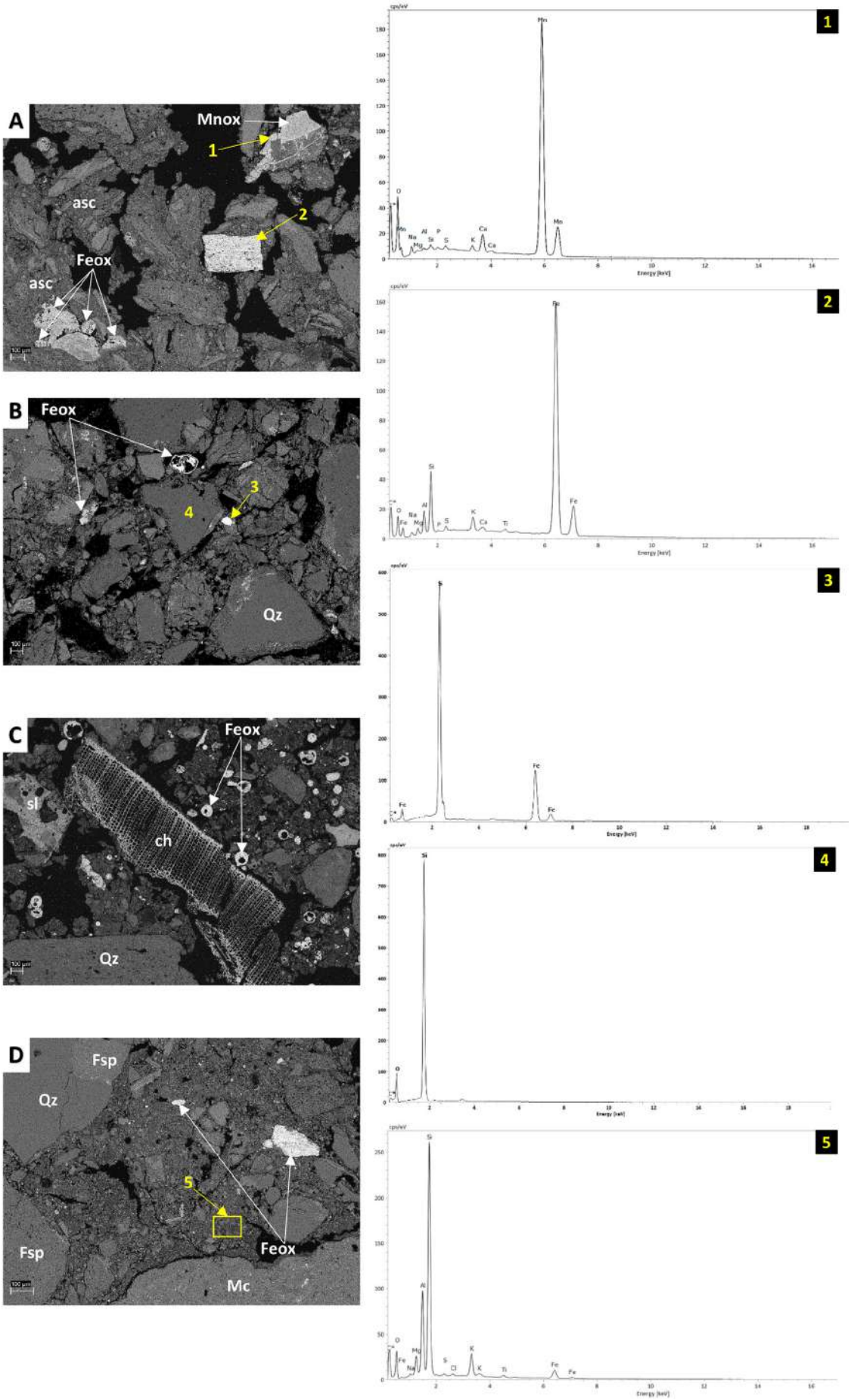


Fig. 2. Soil groundmass features in back-scattered electron (BSE) images and the EDS spectra for selected points or microareas. **A** – profile 1, the transition between C and 2C horizons. The groundmass containing limestone fragments, micromass consisting of aluminosilicate clays (asc) and Fe oxides, Mn oxides (Mnox), and pseudomorphs of Fe oxides (Feox) after sulphides. Voids are black. **B** – profile 6, ABw horizon. Groundmass consisting of quartz (Qz), aluminosilicates (e.g. feldspars), and pseudomorphs of Fe oxides (Feox) after sulphides. Voids are black. **C** – profile 11, the transition between A and C1 horizons. Charcoal (ch) and the groundmass containing slag (sl), quartz (Qz), spherical grains of Fe oxides (Feox) (most likely magnetite), and the micromass rich in clays and humic substances. Voids are black. **D** – profile 4, C1 horizon. Groundmass consisting of quartz (Qz), feldspars (Fsp), micas (Mc), and the micromass with a considerable share of clay minerals. Voids are black

3.2.2. Technosols developed from mine wastes containing granite and gneiss (group II)

Technosols of group II (profiles 5–10) originated from mine wastes comprising igneous (granite) and metamorphic (gneiss) rock fragments. A complex microstructure was dominant in the soils, interspersed with granular aggregates (Fig. 3 A–J) (Table 2). Complex packing voids and simple packing voids occurred between coarse fragments and soil aggregates.

The groundmass had coarse monic c/f related distribution (Table 2). It was composed of soil microaggregates and poorly weathered rock and mineral fragments (Fig. 3G and H). The predominant mineral grains were quartz, muscovite, biotite, fine-grain mica (sericite), chlorite, and Fe oxides (Fig. 3I and J) (Table 2). Fe sulphides were rarely found (Fig. 2B). The micromass was composed most likely of clay minerals and Fe oxides, and it had a yellowish brown colour, as well as undifferentiated and granostriated b-fabric as it was found in ABw horizon in profile 6 (Fig. 3C and D). Well-developed crumb-like aggregates predominated (Fig. 3E and F). Occasional Fe oxide-bearing coatings on rock fragments were observed as it was identified in the transition between A and Bw horizons in profile 5 (Fig. 3A and B). Moreover, bioturbations in the form of channels filled with soil material that was most likely reworked by soil fauna were also found, e.g., in the transition between AC and C1 horizons in profile 8 (Fig. 3G and H).

3.2.3. Technosols containing metallurgical wastes (group III)

Technosols of group III (profiles 11–13) contained metallurgical wastes including slags, as the major soil substrate. The microstructure of these soils was complex with weak granular microaggregates (Fig. 4 A–J) (Table 2). Complex packing voids were present between coarse fragments and soil aggregates.

The groundmass was composed mainly of metallurgical slag fragments with hollows often inhabited by soil organisms (most likely some nematode or enchytraeid) and filled with a soil micromass reworked by these animals, well visible in the transition between A and C1 horizons in profile 11 (Fig. 4A and B). Slags were composed of pyroxene and magnetite (Fig. 4G and H), but some of them were amorphous materials (Fig. 4I and J) (Table 2). Common coarse components in the groundmass were spherical iron oxides, most likely magnetite (Fig. 2C). Micromass was dark brown and black as it contained an admixture of organic carbon. Dark soil colour was related to the abundance of charcoal fragments, noted e.g. in profile 11, the transition between A and C1 horizon (Fig. 2C), and organic matter of anthropogenic origin dispersed in the micromass. Transformed plant residues were occasionally found in the soils. Brownish aggregates composed of allochthonous clay mineral-bearing soil material were found in profile 11, C2 horizon, and in profile 12, A horizon (Fig. 4C–F). These aggregates most likely originated from mixing local native soil with anthropogenic material formed during smelting activity.

3.2.4. Technosols developed from mine wastes having the features of group I and II soils

Parent material of profile 4 was a mixture of carbonate sedimentary rocks, igneous, and metamorphic rocks. The soil substrate was characterised by subangular blocky microstructure (Fig. 5 A–D) (Table 2). Complex packing voids and smooth planar voids were the most common void types.

The groundmass showed two types of soil micromass: yellowish brown and reddish brown. Groundmass had porphyric c/f related distribution and undifferentiated b-fabric (Fig. 5 A–D). It consisted of aluminosilicate clays with an admixture of Fe oxides (Fig. 2D). Coarse material was represented by fragments of quartz, feldspars, carbonates, micas (Fig. 5A and B; Table 2), and Fe oxides (Fig. 2D). Organic matter consisted of dark brown organic residues dispersed in micromass and channels. Channels were often filled with roots (Fig. 5C and D).

3.3. SEM-EDS analyses

Detailed examination of soil material in group I revealed the presence of a pseudomorph of Fe oxides after sulphides in the transition between C and 2C horizons in profile 1 (Fig. 6). This pseudomorph was composed entirely of Fe oxides. Based on the crystal habit, it can be supposed that this pseudomorph was formed due to the weathering of primary Fe sulphides. The pseudomorph was surrounded by rock fragments composed of aluminosilicates (feldspars, micas). Fragments of carbonate minerals were dispersed in the soil micromass composed of aluminosilicate clays and Fe oxides. Moreover, a coating of secondary Ca carbonates was found on the surface of a feldspar grain (Fig. 6).

SEM-EDS analyses of a groundmass in profile 8 (the transition between AC and C1 horizons), representing group II Technosols, showed that rock fragments were composed of aluminosilicates, quartz, and Fe oxides (Fig. 7). The groundmass contained coarse components: aluminosilicates (feldspars, micas, chlorite), quartz, and barite. The peaks of Ti–Kα (4.51 keV) and Ba–Lα (4.47 keV) in the EDS spectra partially overlapped; however, careful comparison of EDS maps for Ti and Ba enabled a clear distinction between Ba-bearing and Ti-bearing phases (Ti-bearing minerals in the soil groundmass are indicated by the red colour in the EDS map for Ti) (Fig. 7). Soil micromass was composed of aluminosilicate clays. The map for Mn revealed the occurrence of coatings composed of Mn-bearing phases (most likely Mn oxides). The coatings occurred on both rock fragments and seem to be pedogenic in origin.

The soil material in profile 11 (the transition between A and C1 horizons) representing group III is presented in Fig. 8. It was composed of slag and quartz fragments and the groundmass between these fragments. The slag consisted mainly of Fe, Al, K, and Ca, and contained acicular Fe-bearing phases (most likely Fe oxides). The groundmass contained quartz, aluminosilicates (most likely feldspars and micas), and Fe oxide spherules as coarse components. The micromass was likely composed of aluminosilicate clays, but also contained a remarkable contribution of S and P, suggesting the occurrence of organic compounds. The elemental map for S (Fig. 8) revealed the presence of a coating containing S-bearing compounds, most likely some sulphates.

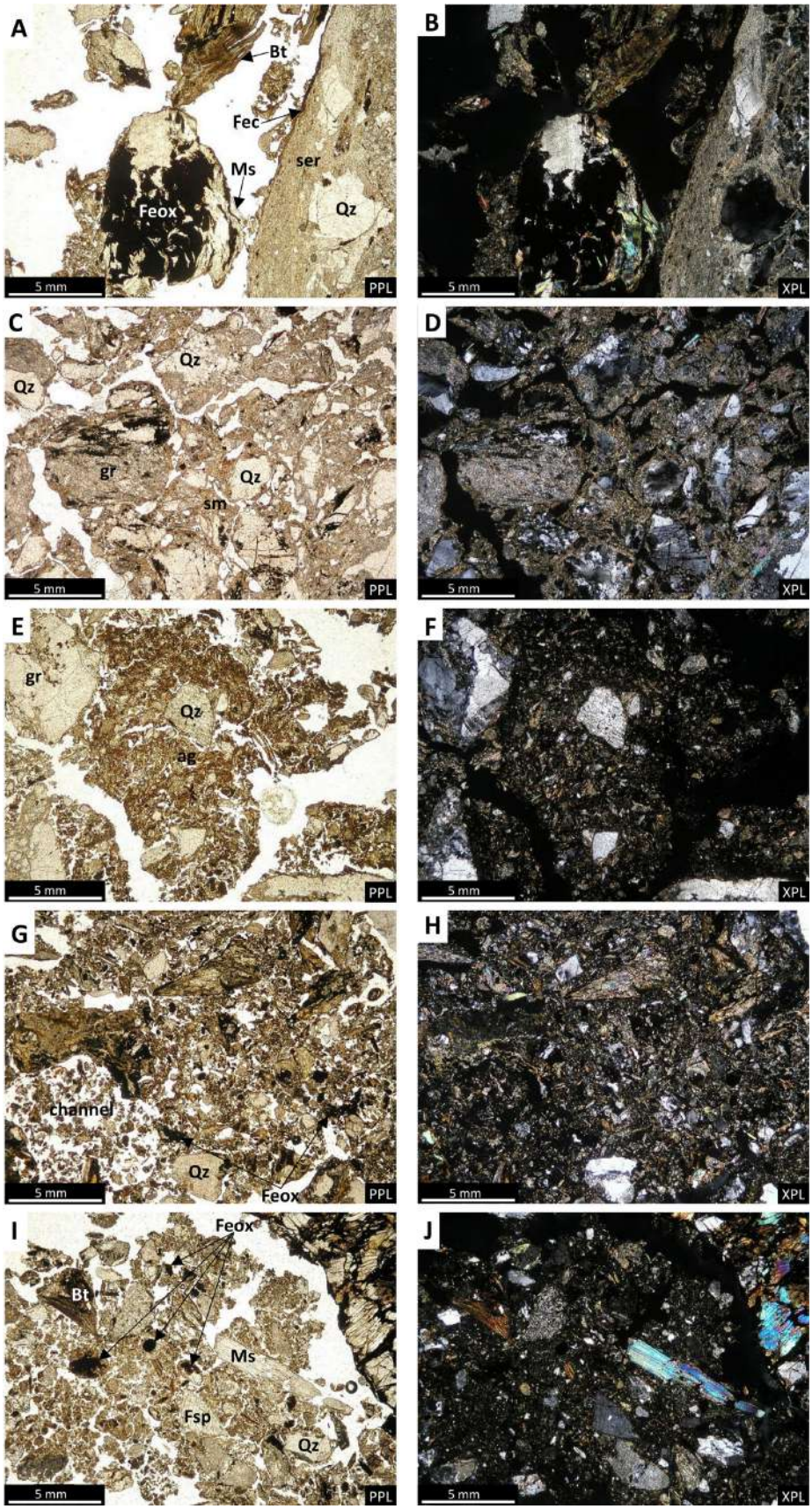


Fig. 3. Micromorphological features of Technosols developed from mine wastes comprising igneous and metamorphic rocks (granite and gneiss) (group II). **A and B** – profile 5, transition between A and Bw horizons. Rock fragments composed of quartz (Qz), muscovite (Ms), biotite (Bt), fine-grain mica (sericite) (ser), and Fe oxides (Feox), accompanied by soil material. Note the occurrence of a Fe oxide-bearing coating (Fec) on a rock fragment. **C and D** – profile 6, ABw horizon. The granite (gr) fragment, quartz grains (Qz), and the soil micromass (sm) composed of clay minerals and Fe oxides exhibiting granostriated b-fabric and surrounding rock fragments and mineral grains. **E and F** – profile 6, ABw horizon. Brown soil aggregate (ag) composed of micromass containing clay minerals and Fe oxides, as well as granite fragments (gr) and quartz (Qz) grains. **G and H** – profile 8, the transition between AC and C1 horizons. Groundmass composed of soil microaggregates and poorly weathered rock and mineral fragments (quartz – Qz, Fe oxides – Feox). Note the occurrence of a channel (bottom left) filled with soil material that is most likely reworked by soil fauna. **I and J** – profile 9, AC horizon. A groundmass consisting of feldspars (Fsp), quartz (Qz), muscovite (Ms), biotite (Bt), Fe oxides (Feox) as well as brown soil micromass characterized by undifferentiated b-fabric and composed of clay minerals and Fe oxides. Explanations: PPL – plane-polarized light, XPL – crossed polarizers

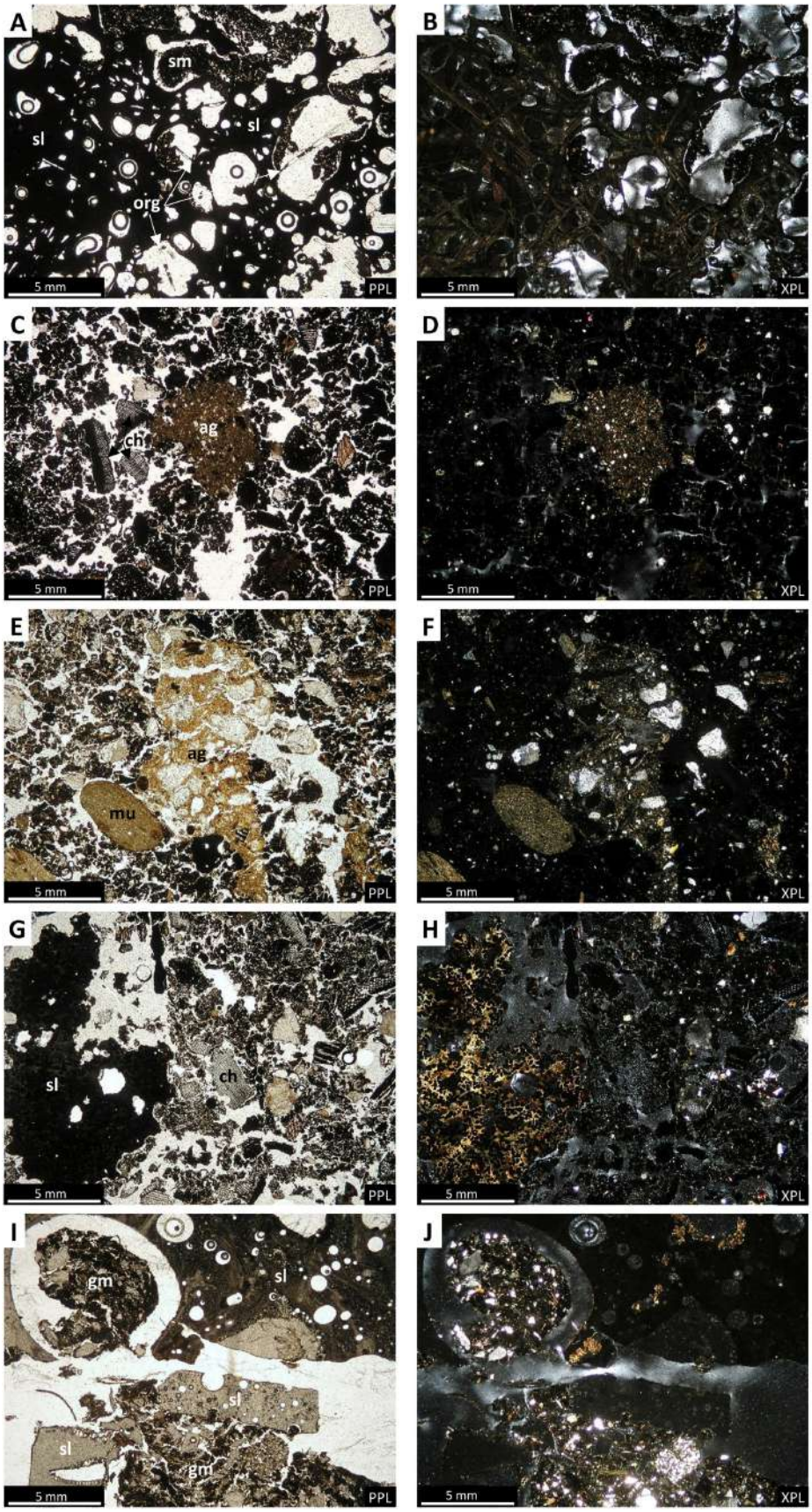


Fig. 4. Micromorphological features of Technosols developed in historical smelting areas (group III). **A and B** – profile 11, the transition between A and C1 horizons. A black metallurgical slag (sl) fragment with hollows partly inhabited by elongated tubular soil organisms (most likely some Nematoda or Enchytraeidae) (org); hollows are filled with a soil micromass (sm) reworked by these animals. **C and D** – profile 11, C2 horizon. Brownish aggregate (ag) composed of soil material surrounded by a dark material containing charcoals (ch) and the organic matter of anthropogenic origin. Brownish aggregate most likely originated from mixing local soil with anthropogenic material formed during smelting activity. **E and F** – profile 12, A horizon. Brownish aggregate (ag) composed of soil material and rounded mudstone (mu) fragment surrounded by a dark material containing organic matter of anthropogenic origin. Brownish aggregate most likely originated from mixing local soil with anthropogenic material formed during smelting activity. **G and H** – profile 12, 2C horizon. A slag (sl) fragment composed of pyroxene and magnetite, charcoals (ch), and a dark material rich in organic matter of anthropogenic origin. **I and J** – profile 13, AC horizon. Slag (sl) fragments and the groundmass (gm) being a mixture of dark organic matter, rock fragments, and mineral grains. Explanations: PPL – plane-polarized light, XPL – crossed polarizers

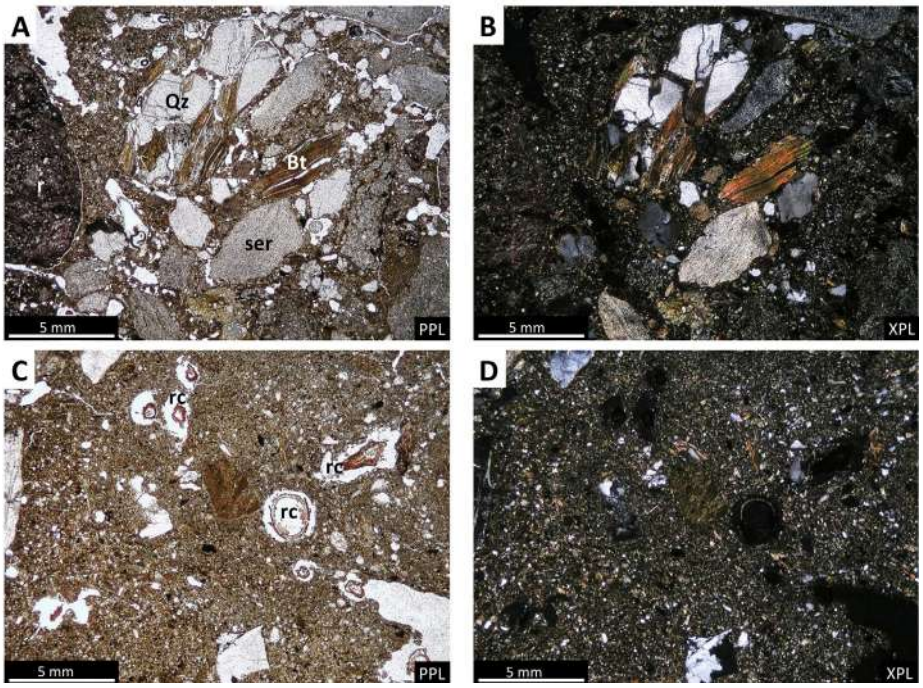


Fig. 5. Micromorphological features of Technosol having features of group I and II (profile 4). **A and B** – C1 horizon. Two types of soil micromass with Fe oxides surrounding different rock (r) fragments and mineral grains, e.g. quartz (Qz), biotite (Bt), and fine-grain mica (sericite) (ser). **C and D** – C1 horizon. Soil micromass consisting of clay minerals and Fe oxides having root channels (rc) filled with plant tissues. Explanations: PPL – plane-polarized light, XPL – crossed polarizers

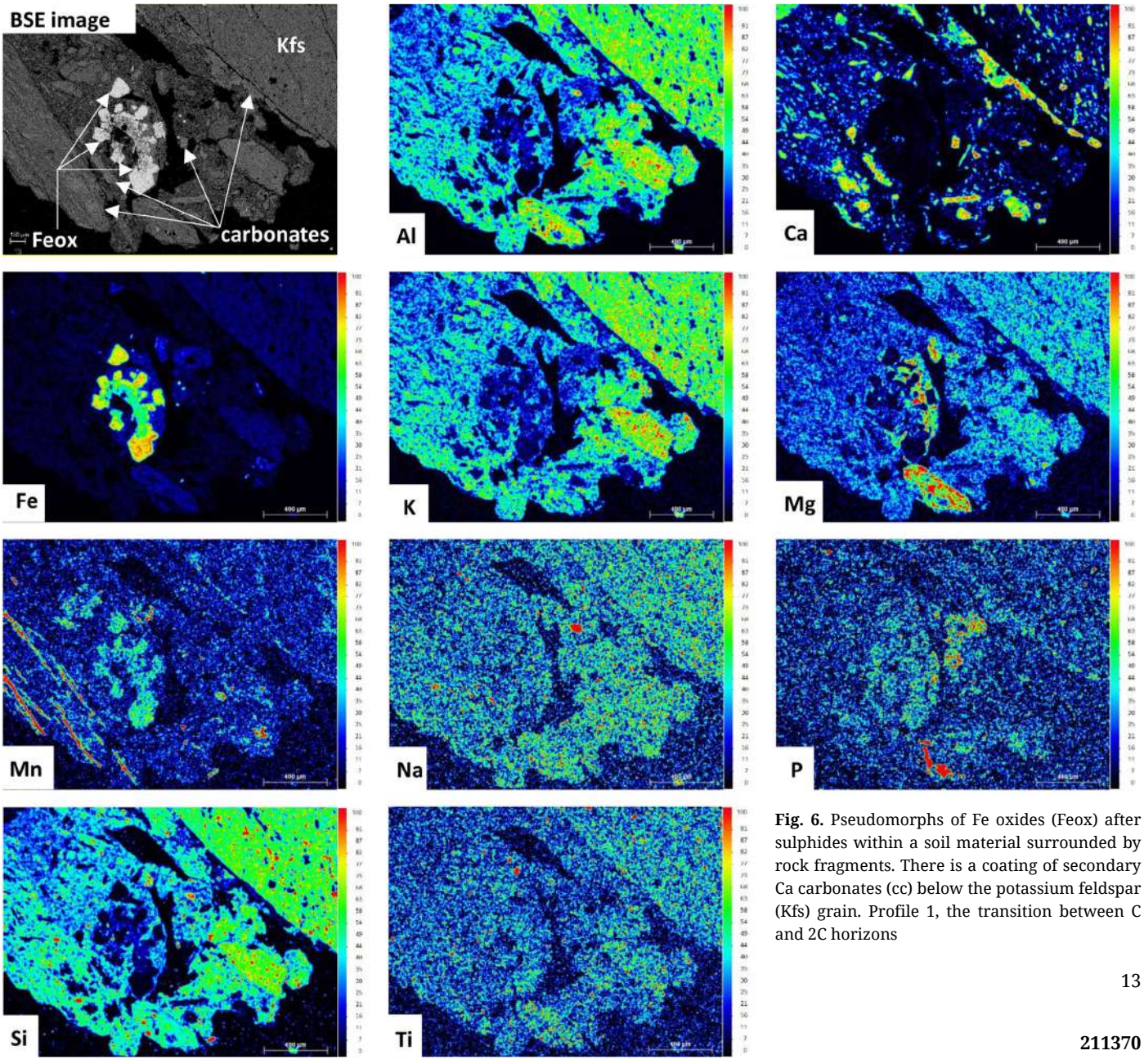


Fig. 6. Pseudomorphs of Fe oxides (Feox) after sulphides within a soil material surrounded by rock fragments. There is a coating of secondary Ca carbonates (cc) below the potassium feldspar (Kfs) grain. Profile 1, the transition between C and 2C horizons

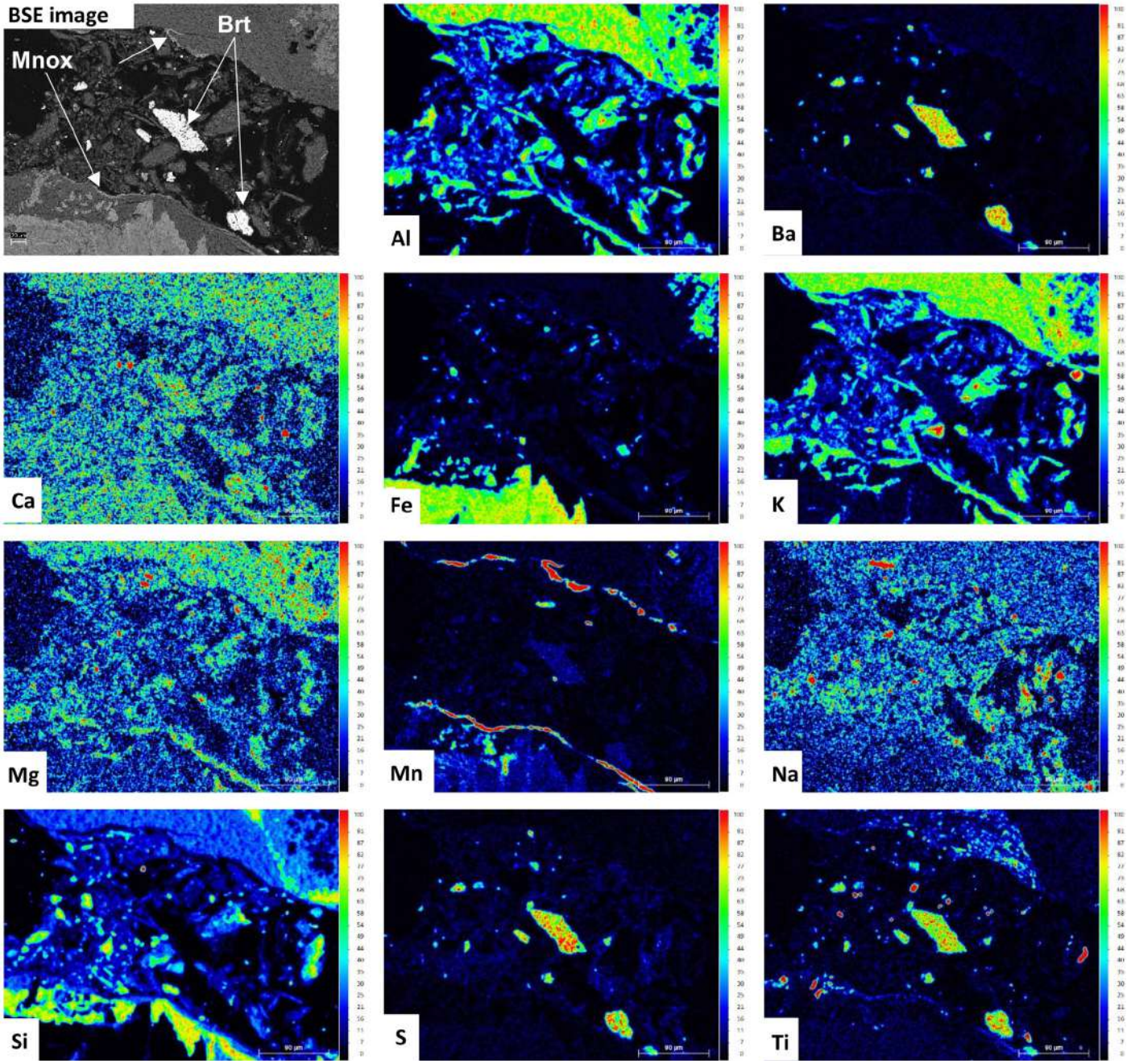


Fig. 7. A space between two rock fragments filled with fine grains of aluminosilicates and barite (Brt). Surfaces of rock fragments are covered with coatings composed of Mn oxides (Mnox). Profile 8, the transition between AC and C1 horizons

3.4. Pedogenic forms of Fe, Al, Si, and Mn

The Fe_t contents ranged from 7484 to 344307 mg·kg^{-1}, Fe_d from 1273 to 50639 mg·kg^{-1} and Fe_{ox} from 499 to 93449 mg·kg^{-1} across all profiles (Table 3). The analysis of pedogenic forms revealed distinct differences in the Fe_d/Fe_t and Fe_{ox}/Fe_d ratios across the studied profiles. In profiles 1 to 3 representing soils derived from carbonate rock mine wastes (group I), the Fe_d/Fe_t and the Fe_{ox}/Fe_d ratios averaged 0.38 and 0.22, respectively. Profile 3 showed clearly higher Fe_{ox}/Fe_d values (0.53 on average), indicating distinct chemical characteristics or more advanced effects of the soil-forming process in profile 3. In profiles 5 to 10 representing soils derived from aluminosilicate igneous and metamorphic rock mine waste (group II), the Fe_d/Fe_t and Fe_{ox}/Fe_d ratios averaged 0.32 (Table 3). The content of Fe_{ox} averaged 3531 mg·kg^{-1} and the content of Fe_d averaged 13519 mg·kg^{-1} in these profiles. In profile 4 having characteristics of groups I and II, the Fe_d/Fe_t ratio and the Fe_{ox}/Fe_d ratio averaged 0.41 and 0.18, respectively. Profiles 11 and 12 representing soils containing metallurgical wastes (group III), showed exceptionally high Fe_t content (192591 mg·kg^{-1} on average) (Table 3). The Fe_d/Fe_t ratio averaged 0.25 in profiles 11 and 12. Moreover, the content of Fe_{ox}

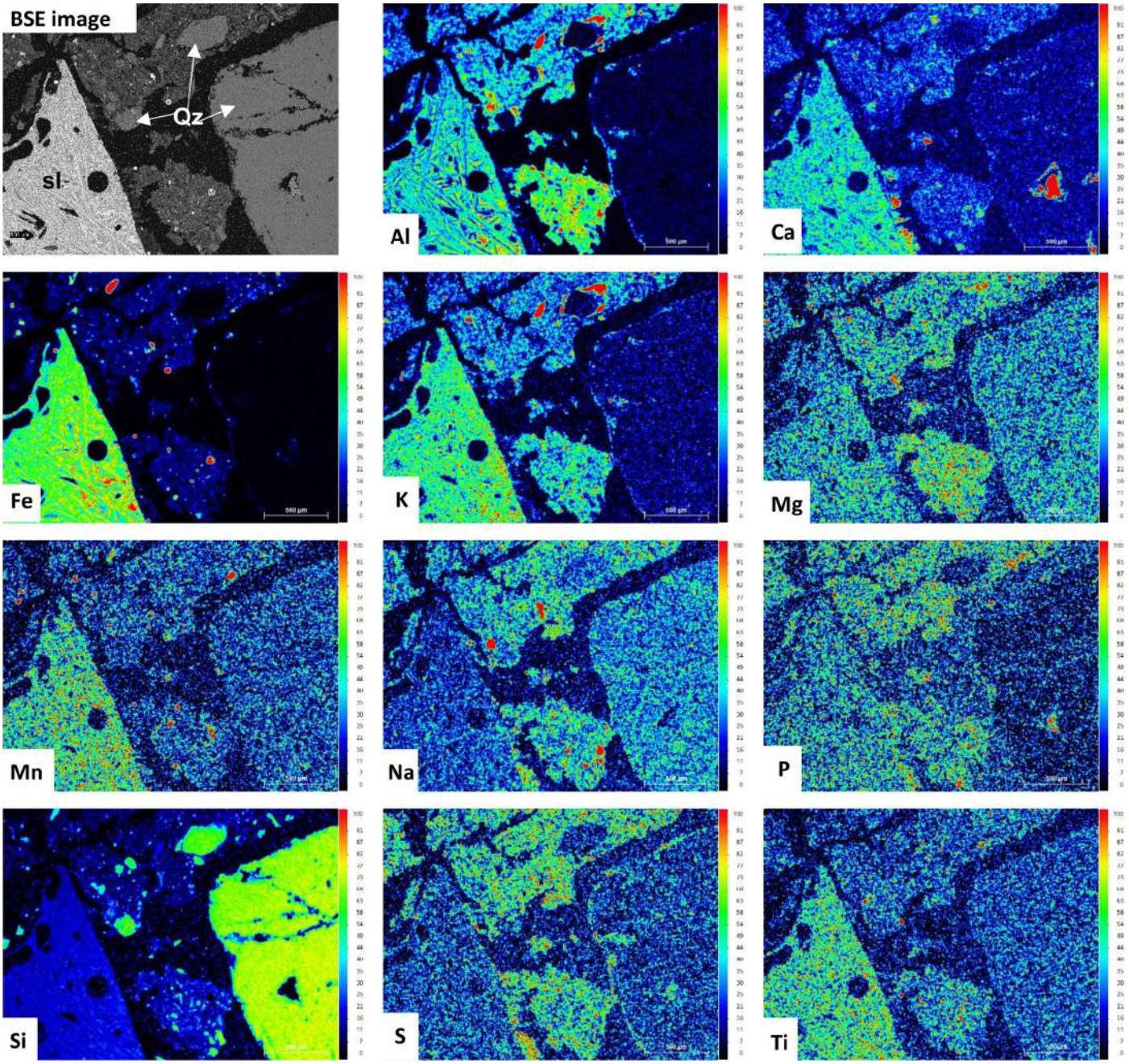


Fig. 8. A slag (sl) fragment composed mainly of Fe, K, Al, Ca, Mn, Ti, and the quartz (Qz) grain surrounded by the groundmass containing mainly Al, K, Mg, Na, S, and P. Note the occurrence of a coating containing S around the quartz grain. Profile 11, the transition between the A and C1 horizons

(57452 mg·kg^{-1} on average) was higher than the concentrations of Fe_d (39388 mg·kg^{-1} on average) in these profiles. Consequently, the Fe_{ox}/Fe_d ratio was high in profiles 11 and 12 (1.40 on average). Profile 13, also representing group III, exhibited a lower Fe_d/Fe_t ratio, averaging 0.16, with Fe_{ox}/Fe_d ratio averaging 0.64 (Table 3).

The Al_{ox}, Si_{ox}, and Mn_{ox} concentrations varied across the profiles (Table 3). In group I (profiles 1–3), Al_{ox} values averaged 1578 mg·kg^{1}, Si_{ox} 225 mg·kg^{-1}, and Mn_{ox} 17699 mg·kg^{-1}. In group II, Al_{ox}, Si_{ox}, and Mn_{ox} contents averaged 1747, 156, and 2136 mg·kg^{-1}, respectively. Profile 4 exhibited the following mean values for Al_{ox} (1018 mg·kg^{-1} on average), Si_{ox} (147 mg·kg^{-1} on average), and Mn_{ox} (563 mg·kg^{-1} on average). In group III, Al_{ox} content averaged 3298 mg·kg^{-1}, Si_{ox} 3565 mg·kg^{-1}, and Mn_{ox} 3758 mg·kg^{-1} (Table 3).

The content and distribution of Al_{ox} + ½Fe_{ox} varied across the profiles (Table 3). In group I (profiles 1–3), Al_{ox} + ½Fe_{ox} values were generally low, averaging 0.23%. In group II (profiles 5–10), Al_{ox} + ½Fe_{ox} values averaged 0.35%, while among profiles 5 and 6, the highest values occurred in Bw and ABw horizons. In group III (profiles 11–13), Al_{ox} + ½Fe_{ox} exhibited the highest values, averaging 2.70%. Profile 4 demonstrated a relatively low Al_{ox} + ½Fe_{ox}, averaging 0.20% (Table 3).

Table 3
Forms of Fe, Al, Si, and Mn in the studied Technosols

Profile	Horizon	Depth	Fe_t	Fe_d	Fe_{ox}	Al_{ox}	Si_{ox}	Mn_{ox}	$Fe_t - Fe_d$	$Fe_d - Fe_{ox}$	Fe_d/Fe_t	Fe_{ox}/Fe_d	$Al_{ox} + ½Fe_{ox}$
			$mg \cdot kg^{-1}$										(%)
Profile 1	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	AC1	1–5	32168	11840	1076	1182	241	30043	20328	10764	0.37	0.09	0.17
	AC2	5–15	32290	10957	758	928	188	31838	21333	10199	0.34	0.07	0.13
	C	15–35	32933	19117	632	761	236	28362	13817	18484	0.58	0.03	0.11
	2C	35–60	43989	12140	804	783	255	4510	31849	11336	0.28	0.07	0.12
Profile 2	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	AC1	1–25	32543	13169	884	1109	273	26917	19374	12285	0.40	0.07	0.16
	AC2	25–45	51424	14065	764	1031	300	28831	37360	13301	0.27	0.05	0.14
	AC3	45–65	47192	14539	877	1105	301	29762	32653	13662	0.31	0.06	0.15
	2C	65–90	48343	12201	4963	3289	447	13915	36142	7238	0.25	0.41	0.58
Profile 3	Oe	0–6	–	–	–	–	–	–	–	–	–	–	–
	O/C	6–25	7484	3265	1865	1888	70	141	4219	1400	0.44	0.57	0.28
	AC	25–40	10352	5191	2789	2565	83	184	5160	2402	0.50	0.54	0.40
	BC	40–60	12100	5502	2650	2719	80	189	6598	2852	0.45	0.48	0.40
Profile 4	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	A	1–13	19396	8545	2490	1371	147	344	10851	6055	0.44	0.29	0.26
	C1	13–35	31553	12213	1446	836	148	623	19340	10767	0.39	0.12	0.16
	C2	35–60	33188	13115	1780	848	146	723	20073	11334	0.40	0.14	0.17
Profile 5	Oe	0–3	–	–	–	–	–	–	–	–	–	–	–
	Oa	3–10	–	–	–	–	–	–	–	–	–	–	–
	A	10–15	35965	11425	4766	1152	63	449	24539	6659	0.32	0.42	0.35
	Bw	15–20	47532	10233	5522	1116	106	1267	37298	4711	0.22	0.54	0.39
	C	20–45	43194	7461	4460	542	156	1115	35733	3001	0.17	0.60	0.28
Profile 6	Oe	0–2	–	–	–	–	–	–	–	–	–	–	–
	Oa	2–10	–	–	–	–	–	–	–	–	–	–	–
	ABw	10–20	37929	8986	4928	1438	128	1542	28943	4058	0.24	0.55	0.39
	C	20–65	37223	7758	3974	340	130	990	29464	3785	0.21	0.51	0.23
Profile 7	Oe	0–2	–	–	–	–	–	–	–	–	–	–	–
	AC	2–15	30094	10122	7170	4478	138	226	19972	2952	0.34	0.71	0.81
	C	15–50	38044	9407	2962	4006	469	910	28637	6445	0.25	0.31	0.55
Profile 8	Oe	0–4	–	–	–	–	–	–	–	–	–	–	–
	AC	4–15	45015	19289	2035	613	37	2125	25726	17254	0.43	0.11	0.16
	C1	15–35	46457	17182	1781	625	54	4521	29275	15400	0.37	0.10	0.15
	C2	35–55	45016	19709	1298	723	45	3867	25307	18410	0.44	0.07	0.14
Profile 9	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	AC	2–10	42267	17032	2056	1265	95	2986	25235	14976	0.40	0.12	0.23
	C1	10–40	45117	15404	2462	2639	321	3549	29714	12942	0.34	0.16	0.39
	C2	40–80	44167	16350	1950	2119	250	3487	27817	14400	0.37	0.12	0.31

Table 3 – continue

Profile	Horizon	Depth	Fe_t	Fe_d	Fe_{ox}	Al_{ox}	Si_{ox}	Mn_{ox}	$Fe_t - Fe_d$	$Fe_d - Fe_{ox}$	Fe_d/Fe_t	Fe_{ox}/Fe_d	$Al_{ox} + ½Fe_{ox}$
			mg·kg^{-1}										(%)
Profile 10	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	AC	1–10	46208	16665	2273	1358	103	2209	29543	14392	0.36	0.14	0.25
	C1	10–50	43335	14692	3588	2190	161	2473	28642	11104	0.34	0.24	0.40
	C2	50–70	41660	14588	5273	3346	244	2458	27073	9314	0.35	0.36	0.60
Profile 11	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	A	1–15	150180	44380	55275	3131	2933	3298	105801	–10895	0.30	1.25	3.08
	C1	15–30	166565	50639	71156	3474	3694	5656	115926	–20517	0.30	1.41	3.91
	C2	30–45	286041	48733	86147	4359	6149	5716	237308	–37414	0.17	1.77	4.74
	C3	45–60	311685	41840	90804	4369	5648	3500	269845	–48964	0.13	2.17	4.98
Profile 12	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	A	1–20	189182	47390	74844	3680	2845	2876	141792	–27454	0.25	1.58	4.11
	C1	20–28	39962	12751	16693	1703	510	880	27211	–3942	0.32	1.31	1.00
	2C	28–50	344307	49050	93449	3810	4405	2142	295257	–44400	0.14	1.91	5.05
	3C	50–60	217413	49395	20469	500	1346	2649	168018	28926	0.23	0.41	1.07
	4C	60–75	27981	10311	8232	1407	324	500	17670	2079	0.37	0.80	0.55
Profile 13	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–
	AC	1–15	16008	3690	3256	9615	11146	13961	12318	434	0.23	0.88	1.12
	2C	15–25	13457	1273	499	232	217	156	12184	774	0.09	0.39	0.05

Explanations: – not determined; Al_{ox} – oxalate-extractable Al; Fe_d – dithionite-extractable Fe; Fe_d/Fe_t – Fe oxide mobility index; Fe_{ox} – oxalate-extractable Fe; Fe_{ox}/Fe_d – Fe oxide activity index; Fe_t – total content of Fe; Mn_{ox} – oxalate-extractable Mn; Si_{ox} – oxalate-extractable Si.

4. Discussion

4.1. Micromorphological and submicromorphological indicators of pedogenesis

The Technosols studied were soils representing an initial stage of advancement of soil-forming processes, which is corroborated by a poor development of soil profiles. However, microscale effects of pedogenic transformation and reorganisation of soil substrate can be distinguished in these soils, which can be treated as micromorphological indicators of pedogenesis. These indicators show that despite the young age of soils (approximately 200–500 years) and poor soil profile development, the weathering, soil-forming, and biological processes transform technogenic mineral substrate into a functioning soil. The following micromorphological effects of pedogenesis were identified in the investigated Technosols: (1) sulphide weathering and formation of Fe oxide pseudomorphs after sulphides; (2) formation of pedogenic structure; (3) formation of pedogenic carbonate coatings in soils developed from mine wastes composed of carbonate rocks; (4) formation of pedogenic Fe and Mn oxide coatings in acidic soils developed from mine wastes composed of crystalline rocks (granite, gneiss); (5) formation of pedogenic sulphate coatings in soils containing metallurgical wastes, and (6) bioturbations and the formation of a soil material reworked by soil animals within biogenic channels.

The occurrence of Fe oxide pseudomorphs after sulphides (Fig. 2A and B; Fig. 6), particularly in profiles containing primary sulphides (i.e. in profiles 1–10), is clear evidence of active chemical weathering, which is the most important process involved in the transformation of Fe sulphides in the studied soils. This process was previously identified in Technosols (e.g. Néel et al., 2003; Uzarowicz and Skiba, 2011; Uzarowicz et al., 2024), and is expressed by the development of pseudomorphs due to the gradual in situ transformation of sulphides into Fe oxides through the oxidation of sulphides, accompanied by the release of sulphate ions to the soil solution. It was found in previous studies of Technosol chronosequence that the degree of sulphide transformation and the crystallinity of iron oxides increase with soil age (Uzarowicz, 2013). Both Fe sulphides and Fe oxide pseudomorphs after sulphides were rare components of the studied Technosols in the Tatra Mountains. The majority of pseudomorphs found in these soils were totally composed of Fe oxides, which suggests that Technosols containing primary sulphides (i.e., in profiles 1–10) were well aerated soils. It is due to a considerable content of rock fragments in these soils (Table 1),

which enables the air exchange in the studied soils and the oxidation of sulphides (Hayes et al., 2014).

Micromorphological analysis showed the initial development of soil structure, particularly the aggregation of primary particles into soil aggregates (Figs 1–4). The presence of intergrain microaggregate microstructure between rock fragments in the soil indicates the beginning of pedogenic aggregation in the studied Technosols in the Tatra Mountains. Previous studies show that Technosols originate from technogenic substrates such as coal/lignite combustion ashes or mine wastes, which initially have a firm consistency with little aggregation (Uzarowicz et al. 2018a, 2025; Watteau et al., 2019). Soil structure formation begins in the first few years of soil development (Badin et al., 2009; Séré et al., 2010), primarily in the topsoil, as vegetation emerges on a disposal site and the organic matter accumulates in superficial soil horizons. The accumulation of soil organic matter (SOM) is crucial for the development of stable soil aggregates that improve soil structure (Jangorzo et al., 2013, 2014; Watteau et al., 2019). Ortega et al. (2022) found that between 15 and 40 years, the Technosols exhibit advanced structural development and nutrient content comparable to those of natural soils. Biological processes including plant root growth and fauna activity, promote the formation of soil aggregates and increase soil porosity (Hedde et al., 2019). Moreover, the abundance of Ca and carbonates in Technosols also plays a huge role in the development of soil structure (Uzarowicz et al., 2018b). Calcium is most likely an important structure-forming factor in carbonate-rich Technosols in the Tatra Mountains.

Another indicator of pedogenesis in the investigated Technosols is the formation of pedogenic carbonates. Secondary carbonate coatings were identified both micromorphologically (Fig. 1G and H) and by SEM-EDS in Technosols rich in carbonates occurring originally in mine wastes (Fig. 6). Pedogenic carbonates result from the precipitation of $CaCO_3$ from percolating soil solutions, often following the dissolution of primary carbonates (Zamanian et al., 2016; Kowalska et al., 2020). Pedogenic Ca carbonates were previously found, for example, in Technosols developed from thermal power station ash (Uzarowicz et al., 2017; Uzarowicz et al., 2018a; Konstantinov et al., 2020) and in Technosols developing from iron industry deposits (Huot et al., 2014b). Moreover, pedogenic Cu carbonates were identified in Technosols developed from mine wastes from historical copper mines (Uzarowicz et al., 2024). The occurrence of pedogenic carbonates in technogenic soils is evidence of the weathering of Ca-rich technogenic materials and the crystallisation of secondary carbonates from soil solution.

Distinct Fe oxide coatings on mineral grains and rock fragments were observed in acidic Technosols (Fig. 3A and B). The coatings were frequently found in profiles 5 and 6 in A, Bw, and ABw horizons. Such coatings indicate podzolisation and chemical weathering (Van Ranst et al., 2018) involving mobilisation and subsequent precipitation of Fe oxides and oxyhydroxides. Pedogenic Fe oxide coatings in acidic soils arise through the release of Fe from primary Fe-bearing minerals, Fe oxidation, and the precipitation of Fe oxides and oxyhydroxides (Cornell and Schwertmann, 2003). This process is influenced by biological activity, redox conditions, and soil chemical properties. As a result, Fe oxides accumulate as coatings on soil particles. Fe oxide coatings occurring in Technosols containing Bw horizons indicate that pedogenesis in these soils is so advanced that there are conditions for Fe mobilization and Fe oxide coating formation. Technosols with Bw horizons are located in the Pyszniańska Valley, where mining was carried out most likely in the 15th century (Table 1). Therefore, the formation of Bw horizons containing Fe oxide coatings may be related to a relatively long pedogenesis period (Tarnawczyk et al., 2024).

The Mn oxide coatings, which seem to be pedogenic in origin, although less common, were also identified in acidic Technosols (Fig. 7). The explanation of the formation of Mn oxide coatings in the studied Technosols is difficult. Although Mn oxide/hydroxide minerals (e.g., birnessite) are ubiquitous in soils and sediments (McKenzie, 1989), studies on the formation/synthesis of the manganese minerals as coatings in soils are limited (e.g., Eswaran and Raghu Mohan, 1973; Sullivan and Koppi, 1992; Eren et al., 2014). The interplay of soil pH, redox conditions, and biological activity controls Mn oxide precipitation dynamics in soils (Mayanna et al., 2015). Higher pH generally enhances abiotic Mn oxide precipitation, as it was found in Technosols developing from iron industry deposits (Huot et al., 2014b), whereas at lower soil pH, microbial oxidation often drives Mn oxide formation (Mayanna et al., 2015). Therefore, we hypothesize that the formation of Mn oxide coatings in acidic Technosols in the Tatra Mountains can be related to microbial activity in the soils.

In Technosols containing metallurgical wastes, coatings composed of sulphates were identified on mineral grains (Fig. 8), likely resulting from the release of sulphur during the weathering of metallurgical wastes. This is consistent with a number of studies focused on the effects of weathering of metallurgical slags in environmental conditions (Kierczak et al., 2021). Technosols containing metallurgical wastes were rich in anthropogenic organic matter occurring as charcoals. They are the remnants of past industrial activities related to smelting. Similar findings were presented by Huot et al. (2014a). Although slags are anthropogenic materials (Warchulski et al., 2020), they undergo natural weathering processes similar to weathering of minerals and rocks (Kierczak et al., 2021). Weathering transforms primary crystalline phases and glassy (amorphous) components, altering their mineral and chemical composition over time. Secondary minerals such as carbonates, hydroxides, or sulfate-bearing phases may precipitate as coatings or fill voids in slag particles. Sulphate formation during slag weathering arises from the oxidation of sulphide minerals originally occurring in slags, leading to the generation of sulphate ions that precipitate as secondary sulphate minerals (e.g., gypsum). These sulphates are common weathering products indicative of advanced alteration of metallurgical slags (Kierczak et al., 2021). Moreover, weathering of metallurgical slags leads to the mobilisation of metals such as Zn, Pb, Cu, and As, which can be hazardous to the local environment (Kierczak et al., 2013; Potysz et al., 2018; Tarnawczyk et al., 2025).

Evidence of biological activity, including faunal channels, presence of soil fauna (nematodes or enchytraeids) and roots, was identified in several Technosols under study (Fig. 1A, 3G,

4A, and 5C), in particular those with higher organic matter content or plant residues, which is consistent with previous studies (Arocena et al., 2010). As it was mentioned above, biological factors such as root penetration and bioturbation contribute to the formation of soil structure. Biological colonisation of post-industrial areas including industrial waste disposal sites, accelerates aggregate formation and soil structure differentiation (Santini and Fey, 2016; Domínguez-Haydar et al. 2018; Uzarowicz et al., 2020b). The presence of soil fauna (nematodes or enchytraeids) found in voids in slag particles in Technosols containing metallurgical wastes (Fig. 4A and B) indicates that the slags, which are strongly contaminated with trace elements (e.g. Cu, As and Sb) (Tarnawczyk et al., 2025) and seem to be an unfavourable place for living organisms, can be colonised by fauna and serve as a habitat for soil animals. This is in contrast to previous studies (e.g. Acosta et al., 2011) in which the authors found that the soil fauna is vulnerable to high concentrations of trace elements.

4.2. Selective extractions of Fe, Al, Si, and Mn as chemical indicators of pedogenesis

Analysis of Fe, Al, Si, and Mn forms in the studied Technosols from the Tatra Mountains revealed a great diversity of the forms, depending most likely on the nature of anthropogenic parent material. A similar feature was identified in other Technosols developed from diverse industrial wastes (Uzarowicz and Skiba, 2011; Uzarowicz et al., 2017, 2024, 2025).

Pedogenic forms of Fe and Al in the Spolic Technosols studied indicate that in acidic soils, especially those developed from silicate-derived mining wastes, pedogenic processes lead to the mobilisation of Fe and Al. In acidic soils, increased concentrations of oxalate-extracted forms of Fe and Al were identified, which is characteristic of the initial stages of podzolisation and chemical weathering (McKeague and Day, 1966; Krettek and Rennert, 2021). Such a phenomenon has been documented in studies conducted on technogenic acidic soils, where weathering of primary minerals (e.g., biotite, muscovite, plagioclase) leads to the release of Fe and Al into the soil solution, and subsequent precipitation as amorphous or poorly crystalline oxides and hydroxides (Kalita et al., 2019). Similar results were obtained in studies of Technosols in Poland on historical copper mine dumps in Miedziana Góra and Miedzianka (Uzarowicz et al., 2024) as well as on iron ore mine dumps at Osicowa Góra (Uzarowicz et al., 2025) confirming the beginning of Fe and Al mobilisation at the early stages of pedogenesis.

Very high concentrations of oxalate-extractable Mn were detected in profiles 1 and 2, which is most likely related to a high content of Mn in the parent material. Elevated Mn_{ox} content in the investigated soils may indicate active redox cycles and microbial involvement in the oxidation of Mn (Mayanna et al., 2015). In turn, the mobilisation of silicon (Si_{ox}) is associated with the weathering of primary silicate minerals and the formation of secondary amorphous Si forms, which seem to be typical for the early stages of technogenic soils (Uzarowicz et al., 2024, 2025). Concentrations of oxalate-extractable Al and Si were higher in Technosols containing metallurgical slags than in other soils studied (Table 3). This feature is most likely related to the weathering of slags accompanied by a release of Al and Si from slags. Oxalate-extractable Al and Si release was documented during pedogenesis in Technosols developed from thermal power station ash and slag (Uzarowicz et al., 2017), which reflects mineral transformations of ash and slag in the soil environment.

Very high concentrations of oxalate-extractable Fe (Fe_{ox}) are recorded in Technosols containing metallurgical wastes, especially those containing magnetite-rich slags (profiles 11 and 12). Concentrations of Fe_{ox} in these soils are higher than Fe_d (Table 3), which is an unusual situation in the soil environment. A similar phenomenon was identified in Technosols developed from thermal power station ash (Uzarowicz et al., 2017), where it was shown that high Fe_{ox} content does not always reflect only the presence of pedogenic, amorphous forms of Fe, but may also originate from amorphous Fe present in the parent material or be an artefact of the extraction method in the presence of magnetite. This is a mineral that is partially dissolved during dithionite and oxalate extractions (Walker, 1983; Fine and Singer, 1989; Van Oorschot and Dekkers, 1999). Therefore, once magnetite is present in soil, it is difficult to draw reliable conclusions from selective extractions of Fe.

5. Conclusions

1. Micromorphological observations and selective Fe, Al, Si and Mn extractions confirm the initial effects of pedogenesis in Spolic Technosols in areas of historical mining and smelting in the Tatra Mountains. This shows that soils in human-altered high-mountain environments undergo soil-forming processes and may acquire functional properties and ecological significance within a few centuries of pedogenesis.
2. The occurrence of occasional Fe oxide pseudomorphs after sulphides shows that there are good conditions for sulphide weathering in the studied Technosols due to good soil aeration.
3. Soil structure development in the studied Technosols is influenced by weathering of rocks and mineral transformations, chemical properties (e.g. presence or lack of carbonates), organic matter accumulation in the topsoil, as well as root penetration and bioturbation of fauna.
4. Pedogenic coatings reflect the geochemical properties of the parent materials. In soils developed from carbonate-bearing mine wastes, pedogenic carbonate coatings formed due to partial dissolution of primary carbonates and subsequent recrystallisation. In acidic soils derived from crystalline rocks (granite, gneiss), iron oxide coatings were common in Bw horizons, indicating Fe mobilisation and precipitation as Fe oxyhydroxides, whereas Mn oxide coatings occurred only sporadically and formed most likely due to microbial activity. In soils containing metallurgical slags, sulphate coatings were observed, most likely resulting from slag weathering, sulphur release into the soil solution, and crystallisation of sulphates on mineral grains.

5. Bioturbations were observed in the majority of the studied Technosols. These pedofeatures were represented by root channels and biogenic channels filled with a material reworked by soil animals. Soil animals (most likely nematodes or enchytraeids) were found in voids of metallurgical slag, which indicates favourable conditions for the development of fauna communities in Technosols containing wastes from smelting activities.
6. Selective extraction methods showed the release of oxalate-extractable Mn in soils developed from Mn-bearing ore mine wastes, a slight mobilisation of oxalate-extractable Fe and Al in acidic Technosols developed from aluminosilicate parent material (granite, gneiss), and the release of oxalate-extractable Al and Si in Technosols containing metallurgical slags.

CRediT authorship contribution statement

Magdalena Tarnawczyk: Writing original draft, Writing– review & editing, Visualization, Validation, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Łukasz Uzarowicz:** Writing– original draft, Writing– review & editing, Validation, Supervision, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Artur Pędziwiatr:** Writing– review & editing, Validation, Methodology, Investigation, Conceptualization. **Wojciech Kwasowski:** Writing– review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Science Centre, Poland, under research project no. 2021/41/N/ST10/03129. The Minister of Climate and Environment, as well as the Director of the Tatra National Park (TNP), are acknowledged for the permission to conduct the studies in the TNP. Maria Król and Magdalena Sitarz (TNP), as well as Arletta Kochańska-Jeziorska, are acknowledged for their help in the fieldwork and in finding the literature related to the topic. Jakub Kotowski and Marcin Łącki (Faculty of Geology, University of Warsaw, Poland) are acknowledged for their assistance with SEM-EDS analyses.

References

Acosta, J.A., Martinez-Martinez, S., Faz, A., Mourik, J.M. Van, Arocena, J.M., 2011. Micromorphological and chemical approaches to understand changes in ecological functions of metal-impacted soils under various land uses. Applied and Environmental Soil Science 2011, 521329. https://doi.org/10.1155/2011/521329

Allory, V., Séré, G., Ouvrard, S., 2022. A meta-analysis of carbon content and stocks in Technosols and identification of the main governing factors. European Journal of Soil Science 73(1), e13141. https://doi.org/10.1111/ejss.13141

Arocena, J., Mourik, J.M., Schilder, M., Faz Cano, A., 2010. Initial soil development under pioneer plant species in metal mine waste deposits. Restoration Ecology 18, 244–252. https://doi.org/10.1111/j.1526-100X.2009.00582.x

Badin, A.L., Méderel, G., Béchet, B., Borschneck, D., Delolme, C., 2009. Study of the aggregation of the surface layer of Technosols from stormwater infiltration basins using grain size analyses with laser diffractometry. Geoderma 153, 163–171. https://doi.org/10.1016/j.geoderma.2009.07.022

Castillo Corzo, M., Peña Rodríguez, V., Manrique Nugent, M., Villarreyes Peña, E., Byrne, P., Gonzalez, J.C., Patiño Camargo, G., Barnes, C.H.W., Sánchez Ortiz, J.F., Saldaña Tovar, J., De Los Santos Valladares, L., 2025. Potentially toxic elements and radionuclides contamination in soils from the vicinity of an ancient mercury mine in Huancavelica, Peru. Soil Science Annual 76(2), 204389. https://doi.org/10.37501/soilsa/204389

Charzyński, P., Hulisz, P., Bednarek, R.M. (Eds.), 2013. Technogenic soils of Poland. Torun, Polish Society of Soil Science.

Colombini, G., Auclerc, A., Watteau, F., 2020. Techno-moder: A proposal for a new morpho-functional humus form developing on Technosols revealed by micromorphology. Geoderma 375, 114526. https://doi.org/10.1016/j.geoderma.2020.114526

Cornell, R.M., Schwertmann, U., 2003. The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, Second Edition. Wiley-VCH Verlag.

Díaz-Ortega, J., Rivera-Uria, Y., López-Mendoza, E., Sedov, S., Romero, F., Solleiro-Rebolledo, E., Martínez-Jardines, L.G., 2024. Development of sustainable hydromorphic Technosols within artificial wetlands in mining landscapes: the effects of wastewater and hydrothermal geological materials. Journal of Soils and Sediments 24, 2948–2962. https://doi.org/10.1007/s11368-024-03763-4

Domínguez-Haydar, Y., Castañeda, C., Rodríguez-Ochoa, R., Jiménez, J.J., 2018. Assessment of soil fauna footprints at a rehabilitated coal mine using micromorphology and near infrared spectroscopy (NIRS). Geoderma 313, 135–145. https://doi.org/10.1016/j.geoderma.2017.10.032

Drewnik, M., 2008. Geomorfologiczne uwarunkowania rozwoju pokrywy glebowej w obszarach górskich na przykładzie Tatr. Wydawnictwo UJ. (in Polish)

Drewnik, M., Felisiak, I., Jerzykowska, I., Magiera, J., 2008. The Tatra Mts: rocks, landforms, weathering and soils. Geotourism/Geoturystyka 2(13), 51–74. https://doi.org/10.7494/geotour.2008.13.51

Eren, M., Kadir, S., Zucca, C., Akşit, İ., Kaya, Z., Kapur, S., 2014. Pedogenic manganese oxide coatings (calcium buserite) on fracture surfaces in Tortonian (Upper Miocene) red mudstones, southern Turkey. Catena 116, 149–156. https://doi.org/10.1016/j.catena.2014.01.003

Eswaran, H., Raghu Mohan, G., 1973. The microfabric of petroplinthite. Soil Science Society of America Proceedings 37, 79–82. https://doi.org/10.2136/sssaj1973.03615995003700010027x

Fine, P., Singer, M.J., 1989. Contribution of ferrimagnetic minerals to oxalate- and dithionite-extractable iron. Soil Science Society of America Journal 53, 191–196.

Gradziński, M., Jach, R., Stworzewicz, E., 2001. Origin of calcite-cemented Holocene slope breccias from the Długa Valley (the Western Tatra Mountains). Annales Societatis Geologorum Poloniae 71(2), 105–113.

Grünewald, G., Kaiser, K., Jahn, R., 2007. Alteration of secondary minerals along a time series in young alkaline soils derived from carbonatic wastes of soda production. Catena 71(3), 487–496. https://doi.org/10.1016/j.catena.2007.03.022

Hayes, S.M., Root, R.A., Perdrial, N., Maier, R.M., Chorover, J., 2014. Surficial weathering of iron sulfide mine tailings under semi-arid climate. Geochimica et Cosmochimica Acta 141, 240–257. https://doi.org/10.1016/j.gca.2014.05.030

Hedde, M., Nahmani, J., Séré, G., Auclerc, A., Cortet, J., 2019. Early colonization of constructed Technosols by macro-invertebrates. Journal of Soils and Sediments 19, 3193–3203. https://doi.org/10.1007/s11368-018-2142-9

Hess, M., 1996. Climate. [In:] Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Nature of the Tatra National Park. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 53–68.

Huot, H., Faure, P., Biache, C., Lorgeoux, C., Simonnot, M.O., Morel, J.L., 2014a. A Technosol as archives of organic matter related to past industrial activities. Science of the total Environment, 487, 389–398. https://doi.org/10.1016/j.scitotenv.2014.04.047

Huot, H., Simonnot, M.O., Watteau, F., Marion, P., Yvon, J., De Donato, P., Morel, J.L., 2014b. Early transformation and transfer processes in a Technosol developing on iron industry deposits. European Journal of Soil Science 65, 470–484. https://doi.org/10.1111/ejss.12106

Huot, H., Simonnot, M.O., Morel, J.L., 2015. Pedogenetic trends in soils formed in technogenic parent materials. Soil Science 180(4/5), 182–192. https://doi.org/10.1097/SS.0000000000000135

IUSS Working Group WRB, 2022. World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps. 4th edition. International Union of Soil Sciences (IUSS), Vienna, Austria.

Jangorzo, N.S., Watteau, F., Schwartz, C., 2013. Evolution of the pore structure of constructed Technosol during early pedogenesis quantified by image analysis. Geoderma 207−208, 180−192. https://doi.org/10.1016/j.geoderma.2013.05.016

Jangorzo, N.S., Schwartz, C., Watteau, F., 2014. Image analysis of soil thin sections for a non-destructive quantification of aggregation in the early stages of pedogenesis. European Journal of Soil Science 65(4), 485−498. https://doi.org/10.1111/ejss.12110

Jost, H., 1962. O górnictwie i hutnictwie w Tatrach Polskich. Wyd. Nauk.-Techn. Warszawa, pp. 186. (in Polish)

Jost, H., 2004. Dzieje górnictwa i hutnictwa w Tatrach Polskich. Zakopane. (in Polish)

Kabała, C., Greinert, A., Charzyński, P., Uzarowicz, Ł., 2020. Technogenic soils – soils of the year 2020 in Poland. Concept, properties and classification of technogenic soils in Poland. Soil Science Annual 71(4), 267–280. https://doi.org/10.37501/soilsa/131609

Kalita, P., Dutta, M., Karmakar, R.M., Dutta, S., Deka, B., 2019. Pedogenic distribution of iron and aluminium under different land uses in Golaghat district of Assam. Journal of Pharmacognosy and Phytochemistry 8(3), 2554–2561.

Krettek, A., Rennert, T., 2021. Mobilisation of Al, Fe, and DOM from topsoil during simulated early Podzol development and subsequent DOM adsorption on model minerals. Scientific Reports 11, 19741. https://doi.org/10.1038/s41598-021-99365-y

Kierczak, J., Pietranik, A., Piatak, N.M., 2021. Weathering of Slags. [In:] Piatak N.M., Ettler, V. (Eds.), Metallurgical Slags: Environmental Geochemistry and Resource Potential, The Royal Society of Chemistry, pp. 125–150.

Kierczak, J., Potysz, A., Pietranik, A., Tyszka, R., Modelska, M., Néel, C., Ettler, V., Mihaljevič, M., 2013. Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland). Journal of Geochemical Exploration 124, 183–194. https://doi.org/10.1016/j.gexplo.2012.09.008

Klimaszewski, M., 1996. Geomorphology. [In:] Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Nature of the Tatra National Park. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 97–124.

Konstantinov, A., Novoselov, A., Konstantinova, E., Loiko, S., Kurasova, A., Minkina, T., 2020. Composition and properties of soils developed within the ash disposal areas originated from peat combustion (Tyumen, Russia). Soil Science Annual 71(1), 3–14. https://doi.org/10.37501/soilsa/121487

Komornicki, T., Skiba, S., 1996. Gleby, in: Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Przyroda Tatrzańskiego Parku Narodowego. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 215–229.

Kotański, Z., 1971. Przewodnik geologiczny po Tatrach. Wydawnictwo Geologiczne, Warszawa. (in Polish)

Kowalska, J.B., Zaleski, T., Mazurek, R., 2020. Micromorphological features of soils formed on calcium carbonate-rich slope deposits in the Polish Carpathians. Journal of Mountain Science 17(6), 1310–1332. https://doi.org/10.1007/s11629-019-5829-5

Liberak, M., 1927. Górnictwo i hutnictwo w Tatrach Polskich. Wierchy 5, 13–30. (in Polish)

Mayanna, S., Peacock, C.L., Schäffner, F., Grawundera, A., Mertena, D., Kothec, E., Büchela, G., 2015. Biogenic precipitation of manganese oxides and enrichment of heavy metals at acidic soil pH. Chemical Geology 402, 6–17. https://doi.org/10.1016/j.chemgeo.2015.02.029

McKeague, J.A., Day, J.H., 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Canadian Journal of Soil Science 46(1), 13–22. https://doi.org/10.4141/cjss66-003

McKenzie, R.M., 1989. Manganese oxides and hydroxides. [In:] Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments, Soil Science Society of America. Madison, WI, pp. 439–461.

Mehra, O.P., Jackson, M.L., 1958. Iron oxide removal from soils and clay by a dithionite-citrate system buffered with sodium bicarbonate. Clays and Clay Minerals 7, 317–327. https://doi.org/10.1346/CCMN.1958.0070122

Miechówka, A., Ciarkowska, K., 1998. Mikromorfologiczne formy próchnicy tatrzańskich rędzin próchnicznych i butwinowych. Zeszyty Problemowe Postępów Nauk Rolniczych 464, 161–168. (in Polish)

Mirek, Z., 1996. Antropogenic threats and changes of the nature. [In:] Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Nature of the Tatra National Park. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 595–618.

Néel, C., Bril, H., Courtin-Nomade, A., Dutreuil, J.P., 2003. Factors affecting natural development of soil on 35-year-old sulphide-rich mine tailings. Geoderma 111, 1–20. https://doi.org/10.1016/S0016-7061(02)00237-9

Ortega, J., Sedov, S., Romero, F., Jardines, L., Solleiro-Rebolledo, E., 2022. Chronosequence of Technosols at the Peña Colorada mine in Colima, Mexico: a short-term remediation alternative. Journal of Soils and Sediments 22, 942–956. https://doi.org/10.1007/s11368-021-02990-3

Osika, R., 1987. Budowa geologiczna Polski, t. IV Złoża surowców mineralnych. Wydawnictwo Geologiczne, Warszawa. (in Polish)

Pansu, M., Gautheyrou, J., 2006. Handbook of Soil Analysis. Mineralogical, Organic and Inorganic Methods. Springer Berlin, Heidelberg.

Passendorfer, E., 1996. Geology. [In:] Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Nature of the Tatra National Park. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 69–96.

Piękoś-Mirkowa, H., Mirek, Z., 1996. Zbiorowiska roślinne, in: Mirek, Z., Głowaciński, Z., Klimek, K., Piękoś-Mirkowa, H. (Eds.), Przyroda Tatrzańskiego Parku Narodowego. Tatrzański Park Narodowy, Kraków-Zakopane, pp. 237–274.

Potysz, A., Kierczak, J., Grybos, M., Pędziwiatr, A., van Hullebusch, E.D., 2018. Weathering of historical copper slags in dynamic experimental system with rhizosphere-like organic acids. Journal of Environmental Management 222, 325–337. https://doi.org/10.1016/j.jenvman.2018.05.071

Radwańska-Paryska, Z., Paryski, W.H., 1995. Wielka Encyklopedia Tatrzańska. Wyd. Górskie, Poronin, pp. 1555.

Rączkowska, Z.J., 2019. Human impact in the Tatra Mountains. Cuadernos de investigación geográfica / Geographical Research Letters 45(1), 219–244.

Ruiz, F., Andrade, G.R.P., Sartor, L.R., Santos, J.C.B. dos, Souza Júnior, V.S. de, Ferreira, T.O., 2022. The rhizosphere of tropical grasses as driver of soil weathering in embryonic Technosols (SE-Brazil). Catena 208, 105764. https://doi.org/10.1016/j.catena.2021.105764

Santini, T.C., Fey, M.V., 2016. Assessment of Technosol formation and in situ remediation in capped alkaline tailings. Catena 136, 17–29. https://doi.org/10.1016/j.catena.2015.08.006

Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung. Zeitschrift für Pflanzenernährung und Bodenkunde 105, 194–202.

Séré, G., Schwartz, C., Ouvrard, S., Renat, J.C., Watteau, F., Villemin, G., Morel, J.L., 2010. Early pedogenic evolution of constructed Technosols. Journal of Soils and Sediments 10, 1246–1254. https://doi.org/10.1007/s11368-010-0206-6

Soil Science Division Staff, 2017. Soil Survey Manual. Ditzler, C., Scheffe, K., Monger H.C. (Eds.) USDA Handbook 18. Washington, D.C.

Stoops, G., 2021. Guidelines for analysis and description of soil and regolith thin sections. John Wiley & Sons, 184 p.

Stoops, G., Marcelino, V., Mees, F., 2018. Micromorphological features and their relation to processes and classification: general guidelines and Overview. [In:] Stoops, G., Marcelino, V., Mees, F. (Eds.), Interpretation of Micromorphological Features of Soils and Regoliths. Elsevier, pp. 15–35.

Sullivan, L.A., Koppi, A.J., 1992. Manganese oxide accumulations associated with some soil structural pores. I. Morphology, composition and genesis. Australian Journal of Soil Research 30(4), 409–427. https://doi.org/10.1071/SR9920409

Swęd, M., Uzarowicz, Ł., Duczmal-Czernikiewicz, A., Kwasowski, W., Pędziwiatr, A., Siepak, M., Niedzielski, P., 2022. Forms of metal (loid) s in soils derived from historical calamine mining waste and tailings of the Olkusz Zn–Pb ore district, southern Poland: A combined pedological, geochemical and mineralogical approach. Applied Geochemistry 139, 105218. https://doi.org/10.1016/j.apgeochem.2022.105218

Tarnawczyk, M., Uzarowicz, Ł., Kwasowski, W., Górka-Kostrubiec, B., Pędziwiatr, A., 2024. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. Catena 247, 108521. https://doi.org/10.1016/j.catena.2024.108521

Tarnawczyk, M., Uzarowicz, Ł., Kwasowski, W., Pędziwiatr, A., Martín-Peinado, F.J., 2025. Geochemical features of Technosols developed in historical mining and metallurgical sites in the Tatra Mountains, southern Poland: total contents and BCR fractionation of selected trace elements. Minerals 15, 988. https://doi.org/10.3390/min15090988

Thompson, R., Oldfield, F., 1986. Environmental Magnetism. Allen and Unwin, London. https://doi.org/10.1007/978-94-011-8036-8

Uzarowicz, Ł., 2013. Microscopic and microchemical study of iron sulphide weathering in a chronosequence of technogenic and natural soils. Geoderma 197, 137–150. https://doi.org/10.1016/j.geoderma.2013.01.006

Uzarowicz, Ł., Skiba, S., 2011. Technogenic soils developed on mine spoils containing iron sulphides: Mineral transformations as an indicator of pedogenesis. Geoderma 163(1–2), 95–108. https://doi.org/10.1016/j.geoderma.2011.04.008

Uzarowicz, Ł., Zagórski, Z., Mendak, E., Bartmiński, P., Szara, E., Kondras, M., Oktaba, L., Turek, A., Rogoziński, R., 2017. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part I. Properties, classification, and indicators of early pedogenesis. Catena 157C, 75–89. https://doi.org/10.1016/j.catena.2017.05.010

Uzarowicz, Ł., Kwasowski, W., Śpiewak, O., Świtoniak, M., 2018a. Indicators of pedogenesis of Technosols developed in an ash settling pond at the Bełchatów thermal power station (central Poland). Soil Science Annual 69(1), 49–59. https://doi.org/10.2478/ssa-2018-0006

Uzarowicz, Ł., Skiba, M., Leue, M., Zagórski, Z., Gąsiński, A., Trzciński, J., 2018b. Technogenic soils (Technosols) developed from fly ash and bottom ash from thermal power stations combusting bituminous coal and lignite. Part II. Mineral transformations and soil evolution. Catena 162, 255–269. https://doi.org/10.1016/j.catena.2017.11.005

Uzarowicz, Ł., Charzyński, P., Greinert, A., Hulisz, P., Kabała, C., Kusza, G., Kwasowski, W., Pędziwiatr, A., 2020a. Studies of technogenic soils in Poland: past, present, and future perspectives. Soil Science Annual 71(4), 281–299. https://doi.org/10.37501/soilsa/131615

Uzarowicz, Ł., Wolińska, A., Błońska, E., Szafranek-Nakonieczna, A., Kuźniar, A., Słodczyk, Z., Kwasowski, W., 2020b. Technogenic soils (Technosols) developed from mine spoils containing Fe sulphides: Microbiological activity as an indicator of soil development following land reclamation. Applied Soil Ecology 156, 103699. https://doi.org/10.1016/j.apsoil.2020.103699

Uzarowicz, Ł., Swęd, M., Kwasowski, W., Pędziwiatr, A., Kaczmarek, D., Koprowska, D., Górka-Kostrubiec, B., Pawłowicz, E., Murach, D., 2024. Initial pedogenic processes, mineral and chemical transformations and mobility of trace elements in Technosols on dumps of the former copper mines in Miedziana Góra and Miedzianka, the Świętokrzyskie Mts., south-central Poland. Catena 245, 108293. https://doi.org/10.1016/j.catena.2024.108293

Uzarowicz, Ł., Kwasowski, W., Lasota, J., Błońska, E., Górka-Kostrubiec, B., Tarnawczyk, M., Murach, D., Gilewska, M., Gryczan, W., Pawłowicz, E., Jankowski, P., 2025. Vegetation cover as an important factor affecting the properties and evolution of Spolic Technosols: A case study from a dump of the abandoned iron ore mine in central Poland. Catena 254, 108906. https://doi.org/10.1016/j.catena.2025.108906

Van Oorschot, I.H.M., Dekkers, M.J., 1999. Dissolution behaviour of fine-grained magnetite and maghemite in the citrate-bicarbonate-dithionite extraction method. Earth and Planetary Science Letters 167(3–4), 283–295.

Van Ranst, E., Wilson, M.A., Righi, D., 2018. Spodic Materials. [In:] Stoops, G., Marcelino, V., Mees, F. (Eds.), Interpretation of Micromorphological Features of Soils and Regoliths (Second Edition). Elsevier, pp. 633–662. https://doi.org/10.1016/B978-0-444-63522-8.00022-X

Van Reeuwijk, L.P., 2002. Procedures for soil analysis. Technical Paper 9. ISRIC, Wageningen.

Verrecchia, E.P., Trombino, L., 2021. A Visual Atlas for Soil Micromorphologists. Springer, Cham.

Walker, A., 1983. The effects of magnetite on oxalate- and dithionite-extractable iron. Soil Science Society of America Journal 47, 1022–1026.

Warchulski, R., Szczuka, M., Kupczak, K., 2020. Reconstruction of 16th–17th century lead smelting processes on the basis of slag properties: a case study from Sławków, Poland. Minerals 10(11), 1039. https://doi.org/10.3390/min10111039

Warzyński, H., Sosnowska, A., Harasimiuk, A., 2018. Effect of variable content of organic matter and carbonates on results of determination of granulometric composition by means of Casagrande's areometric method in modification by Prószyński. Soil Science Annual 69(1), 39–48. https://doi.org/10.2478/ssa-2018-0005

Watteau, F., Séré, G., Huot, H., Begin, J.C., Schwartz, C., Qiu, R., Morel, J.L., 2017. Micropedology of SUITMAs. [In:] Levin, M.J., Kim, K.-H.J., Morel, J.L., Burghardt, W., Charzyński, P., Shaw, R.K., IUSS Working Group SUITMA (Eds.), Soils within Cities, Global approaches to their sustainable management: Stuttgart, Germany, Catena Soil Sciences, Schweizerbart Science Publishers, pp. 84−92.

Watteau, F., Huot, H., Morel, J.-L., Rees, F., Schwartz, C., Séré, G., 2018. Micropedology to reveal pedogenetic processes in Technosols. Spanish Journal of Soil Science 8(2), 148–163. https://doi.org/10.3232/SJSS.2018.V8.N2.02

Watteau, F., Jangorzo, N.S., Schwartz, C., 2019. A micromorphological analysis for quantifying structure descriptors in a young constructed Technosol. Boletín de la Sociedad Geológica Mexicana 71(1), 11–20. https://doi.org/10.18268/bsgm2019v71n1a2

Watteau, F., Morel, J.L., Liu, C., Tang, Y., Huot, H., 2025. Technosol micromorphology reveals the early pedogenesis of abandoned rare earth element mining sites undergoing reclamation in south China. Minerals 15(5), 514. https://doi.org/10.3390/min15050514

Wątocki, W., 1950. Żyły mineralne na Ornaku w Tatrach Zachodnich. Annales Societatis Geologorum Poloniae 20(1–2), 11–60. (in Polish)

Woś, B., Tahsin Karimi Nezhad, M., Mustafa, A., Pietrzykowski, M., Frouz, J., 2023. Soil carbon storage in unreclaimed post mining sites estimated by a chronosequence approach and comparison with historical data. Catena 220A, 106664. https://doi.org/10.1016/j.catena.2022.106664

Zaiets, O., Poch, R.M., 2016. Micromorphology of organic matter and humus in Mediterranean mountain soils. Geoderma 272, 83–92. https://doi.org/10.1016/j.geoderma.2016.03.006

Zamanian, K., Pustovoytov, K., Kuzyakov, Y., 2016. Pedogenic carbonates: Forms and formation processes. Earth-Science Reviews 157, 1–17. https://doi.org/10.1016/j.earscirev.2016.03.003

Zanuzzi, A., Arocena, J.M., Van Mourik, J.M., Cano, A.F., 2009. Amendments with organic and industrial wastes stimulate soil formation in mine tailings as revealed by micromorphology. Geoderma 154, 69–75. https://doi.org/10.1016/j.geoderma.2009.09.014

Zasoński, S., Niemyska-Łukaszuk, J., 1977. Soil types of Mt. Zgorzelisko based on chemical and micromorphological properties, Roczniki Gleboznawcze – Soil Science Annual 28(1), 243–261.

Zikeli, S., Jahn, R., Kastler, M., 2002. Initial soil development in lignite ash landfills and settling ponds in Saxony-Anhalt, Germany. Journal of Plant Nutrition and Soil Science 165(4), 530–536. https://doi.org/10.1002/1522-2624(200208)165:4%3C530::AID-JPLN530%3E3.0.CO;2-J

Zwoliński, S., 1984. Wpływ hut zakopiańskich na lasy tatrzańskie. Parki Narodowe i Rezerwaty Przyrody 5(1), 43–50. (in Polish)

Mikromorfologiczne, submikromorfologiczne i chemiczne wskaźniki pedogenezy gleb technogenicznych w rejonach historycznego górnictwa i hutnictwa w Tatrach

Słowa kluczowe:

Gleby technogeniczne
Procesy glebotwórcze
Mikromorfologia gleb
Gleby górskie
Historyczne górnictwo
Historyczne hutnictwo

Streszczenie

Gleby technogeniczne (Technosols) powstałe z odpadów górniczych i hutniczych na obszarach historycznej działalności górniczej i hutniczej podlegają naturalnym procesom wietrzeniowym, glebotwórczym i biologicznym. W niniejszym artykule przedstawiono (1) wyniki badań mikromorfologicznych i submikromorfologicznych uzyskanych z użyciem mikroskopii optycznej i skaningowej mikroskopii elektronowej, a także (2) charakterystykę chemiczną opartą na wynikach selektywnych ekstrakcji pedogenicznych form Fe, Al, Mn i Si w glebach technogenicznych w Tatrach. Celem badań była identyfikacja procesów glebotwórczych zachodzących w tych glebach. Takie podejście pozwala na wgląd w złożoną pedogenezę gleb technogenicznych w środowisku alpejskim w obszarach, na które wpływ miała dawna działalność przemysłowa. Przeanalizowano trzynaście profili glebowych, podzielonych je na trzy grupy: (I) gleby technogeniczne utworzone z odpadów górniczych zawierających skały węglanowe (wapienie i dolomity) zawierające rudy żelaza i manganu, (II) gleby technogeniczne wytworzone z odpadów górniczych stanowiących skały magmowe i metamorficzne (granit, gnejs) z pozostałościami rud polimetalicznych, a także (III) gleby technogeniczne zawierające odpady z działalności hutniczej (np. żużle hutnicze). Analiza cienkich płytek (szlifów) z gleb ujawniła następujące mikroskopowe przejawy procesów glebotwórczych: (1) powstawanie pseudomorfoz tlenku żelaza w wyniku wietrzenia siarczkowego; (2) powstawanie pedogenicznej struktury; (3) tworzenie się pedogenicznych otoczek węglanowych w glebach utworzonych z odpadów górniczych zawierających skały węglanowe; (4) tworzenie się pedogenicznych otoczek zawierających tlenki żelaza i manganu w kwaśnych glebach utworzonych z odpadów górniczych składających się ze skał krystalicznych (granit, gnejs); (5) powstawanie pedogenicznych otoczek siarczanowych w glebach zawierających odpady metalurgiczne oraz (6) bioturbacje (np. kanały korzeniowe i kanały biogeniczne wypełnione materiałem przetworzonym przez faunę glebową). Obserwacje mikromorfologiczne wykazały również, że żużle metalurgiczne w glebach technogenicznych mogą stanowić siedlisko dla fauny glebowej (najprawdopodobniej nicieni lub wazonkowców). Selektywne ekstrakcje pedogenicznych form Fe, Al, Mn i Si wykazały (1) uwalnianie Mn ekstrahowanego szczawianem amonu w glebach wytworzonych z odpadów kopalnianych zawierających pozostałości rud Mn, (2) niewielką mobilizację Fe i Al ekstrahowanego szczawianem amonu w kwaśnych glebach technogenicznych wytworzonych z glinokrzemianowego materiału macierzystego oraz (3) uwalnianie Al i Si ekstrahowanych szczawianem amonu w glebach technogenicznych zawierających żużle hutnicze. Wyniki te wskazują, że technogeniczne materiały macierzyste podlegają procesom wietrzenia, które przekształcają skład mineralny badanych gleb technogenicznych. Niniejsza praca przyczynia się do poszerzenia wiedzy na temat gleb technogenicznych i ich potencjalnych funkcji ekologicznych w regionach górskich. Badania poszerzają również wiedzę na temat rozwoju gleb na obszarach historycznej działalności górniczej i hutniczej w środowisku alpejskim Tatr.

Warsaw, 29.09.2025

Magdalena Tarnawczyk
mtarnawczyk@gmail.com

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Pędziwiatr A., Kwasowski W., 2025. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. Soil Science Annual, 76(3), 211370, my individual contribution to its creation consisted of the major part of the work presented in this publication, including writing original draft, writing– review & editing, visualization, validation, project administration, methodology, investigation, funding acquisition, data curation, conceptualization.

Signature

Warsaw, 29.09.2025

Łukasz Uzarowicz
lukasz_uzarowicz@sggw.edu.pl

Agriculture and Horticulture Discipline Council of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Pędziwiatr A., Kwasowski W., 2025. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. Soil Science Annual 76(3), 211370, my individual contribution to its creation consisted of: writing – original draft, writing – review and editing, validation, supervision, methodology, investigation, funding acquisition, data curation, conceptualization.

Signature

Warsaw, 29.09.2025

Artur Pędziwiatr
artur_pedziwiatr@sggw.edu.pl

Agriculture and Horticulture Discipline Council of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Pędziwiatr A., Kwasowski W., 2025. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. Soil Science Annual 76(3), 211370, my individual contribution to its creation consisted of writing – review and editing, validation, methodology, investigation, conceptualization.

Signature

Pędziwiatr Artur

Warsaw 29.09.2025

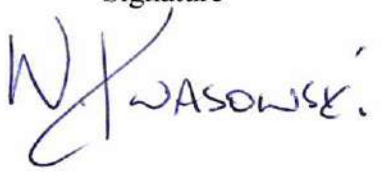
Wojciech Kwasowski
Wojciech_kwasowski@sggw.edu.pl

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Pędziwiatr A., Kwasowski W., 2025. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. Soil Science Annual, my individual contribution to its creation consisted of Writing – review & editing, Validation, Supervision, Methodology, Investigation, Conceptualization.

Signature



minerals

MDPI

Article

Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland

Magdalena Tarnawczyk [1,*], Łukasz Uzarowicz [1], Wojciech Kwasowski [1], Artur Pędziwiatr [1] and Francisco José Martín-Peinado [2]

[1] Department of Soil Science, Institute of Agriculture, Warsaw University of Life Sciences—SGGW, Nowoursynowska Str. 159, Building no. 37, 02-776 Warsaw, Poland
[2] Departamento de Edafología y Química Agrícola, Facultad de Ciencias, Universidad de Granada, Campus de Fuentenueva, s/n, 18071 Granada, Spain
* Correspondence: magdalena_tarnawczyk@sggw.edu.pl

Abstract

Ore mining and smelting are often related to environmental pollution. This study provides information about the geochemical features of Technosols at historical mining and metallurgical sites in the Tatra Mountains, southern Poland, evaluating the contents of potentially toxic trace elements (PTTE) and their behaviours in soils, as well as the influence of soil properties on PTTE mobility. Thirteen soil profiles were studied in eight abandoned mining and smelting sites. PTTE concentrations, including rare earth elements (REE), were measured using ICP-MS and ICP-OES. Selected elements (Cu, Zn, Pb, Cd, As, Sb, Ba, Sr, Co, Ni, Mn and Cr) were fractionated using the modified European Community Bureau of Reference (BCR) four-step sequential extraction. Contamination of soils with PTTE was compared against Polish regulatory limits, which were exceeded for Cu, Zn, Pb, Mo, Hg, As, Co, Ni and Ba, with concentrations exceeding limits by 16, 18, 34 and 160 times for Cu, Hg, As and Ba, respectively, in some profiles. Based on geochemical features depending on parent material properties, the soils examined were divided into three groups. Group I Technosols (near-neutral soils developed from Fe/Mn-ore and carbonate-bearing mining waste) were particularly enriched in Co, Ni, Mn and REE. Group II Technosols (acidic soils developed from polymetallic ore-bearing aluminosilicate mining waste) contained elevated concentrations of Cu, Zn, Hg, As, Sb, Bi, Co, Ag, Ba, Sr, U and Th; they contained lower contents of REE than Group I Technosols. Group III Technosols (soils developed in smelting-affected areas and containing metallurgical waste) were rich in Cu, As, Sb, Ba, Hg, Co and Ag and contained the lowest REE contents among the studied soils. Sequential BCR extraction revealed that PTTE mobility varied strongly according to soil group, with higher mobility of Mn, Cu and Zn in acidic polymetallic ore-derived soils (Group II), while carbonate-rich soils (Group I) showed mainly immobile forms. Metallurgical slag-derived soils (Group III) exhibited complex PTTE behaviour controlled by organic matter and Fe/Mn oxides. Soil properties (pH, carbonates and TOC) seem to control PTTE mobility.

Keywords: technogenic soils; soil contamination; trace elements; rare earth elements; sequential extraction

Academic Editor: Anthimos Xenidis

Received: 15 August 2025
Revised: 4 September 2025
Accepted: 14 September 2025
Published: 17 September 2025

Citation: Tarnawczyk, M.; Uzarowicz, Ł.; Kwasowski, W.; Pędziwiatr, A.; Martín-Peinado, F.J. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. *Minerals* **2025**, *15*, 988. https://doi.org/10.3390/min15090988

1. Introduction

The Tatra Mountains nowadays are known for their rich biodiversity and unique geological and geomorphological features [1]. The area of the Tatra Mountains is now under strict environmental protection as part of Tatra National Park (TNP), which aims to preserve the natural ecosystem. However, the area contains sites affected by historical mining and smelting operations [2,3]. Metals such as Cu, Ag, Fe and Mn were mined and processed at these sites from the 15th century until the end of the 19th century [4–6]. Although nowadays the Tatra Mountains are mainly associated with tourism and natural protection, the area was an important mining region where mines and smelters were developed for centuries. In the 19th century, industrial activities in the Tatra Mountains declined due to the depletion of easily accessible ore deposits, competition from cheaper mines in other regions and rising production costs [2]. Historical mining and smelting in the Tatra Mountains, particularly in Kościeliska Valley, Chochołowska Valley (for example, in the area known as Huciańskie Banie), Pyszniańska Valley, Ornak ridge (including Banisty Żleb and Żleb pod Banie) and Kuźnice, have left a legacy in the form of mining and metallurgical waste deposited on the land surface. Technogenic soils (Technosols) have developed in the superficial parts of waste disposal sites.

Technosols are soils containing artefacts, i.e., materials made, modified or exposed due to human activity that would not otherwise be present on the Earth's surface [7,8]. Mining and metallurgical wastes are common parent materials for Spolic Technosols, which comprise a subgroup of technogenic soils particularly rich in artefacts [9–14]. Vegetation growth on anthropogenic materials can promote their weathering and stimulate the progress of pedogenic processes in post-industrial areas [15,16]. In recent years, the first information about Technosols in the Tatra Mountains was published [17–19]. These studies focused on the determination of soil properties as well as their mineral and chemical composition to classify the soils and identify the first effects of soil-forming processes contributing to their development.

Mining and metallurgical wastes, as well as Technosols developing from these wastes, often contain high concentrations of potentially toxic trace elements (PTTE) (e.g., Cu, Zn, Pb, Cd and As), which can be harmful to plants, animals and humans [20–26]. Contamination of Technosols developed from these wastes is a significant environmental problem due to the possible release of PTTE into the environment [27]. The mobility of PTTE in post-mining soils is affected by various factors, including soil pH, redox conditions, quantity and quality of soil organic matter (SOM), mineral composition of waste and the specific nature of the PTTE [28–30].

Studies on the determination of PTTE in soils in various areas of the Tatra Mountains have been conducted by numerous researchers. Differences in the contents of trace elements in soils around Morskie Oko and Kasprowy Wierch in the TNP with increasing altitude were studied [31]. Research on trace element pollution in Polish national parks, including the TNP, investigated the presence of trace elements in spruce (*Picea abies* (L.) H. Karst) stands, accumulation on the surface and inside the needles, as well as the concentration of bioavailable trace elements in the soil [32]. The influence of spruce and other tree species' habitat types on the nature and occurrence of selected elements was also studied [33]. Moreover, the bioavailability of elements in TNP soils in Chochołowska, Kościeliska, Strążyska and Mała Łąka Valleys was examined [34]. Besides determining the activity of selected radionuclides, the contents of trace elements in the topsoil from Chochołowska, Kościeliska, Bystra, Suchej Wody and Rybiego Potoku Valleys were also investigated [35,36]. The trace element contents in podzols was the subject of further studies [37,38]. Furthermore, trace elements in TNP's initial soils (regosols and leptosols) were analysed [39–41]. Trace element contents were also examined in peat-bog and fen soils [42]

and in soils from grazed mountain glades in the TNP [43]. Recently, forms of elements in soil were determined by comparing the co-occurrence of special forms of metals in forest areas of the TNP [44]. Trace elements were also investigated in selected non-forest soils of the TNP [45,46]. Metal contamination in dustfall, nettle and soils in Chochołowska and Strążyska Valleys and near Morskie Oko, reflecting the impact of long-term trace element emissions, was also assessed [47]. In recent studies, concentrations of trace metals (Zn, Pb and Cd) were analysed in the uppermost layers of non-forest soils from the TNP, with soil surface horizon samples and bedrock samples collected from the bottom of excavation pits [48]. According to research conducted in Slovakia, the most serious soil contaminants in the TNP were Cd and Fe, with transport and tourism identified as the main pollution sources. Although the contents of some PTTE decreased with increasing altitude, this trend could not be unequivocally confirmed [49].

Although the knowledge about the contents of PTTE in soils of the Tatra Mountains is extensive, until now there have not been many studies focusing on PTTE in soils of historical mining and smelting areas, including sites where post-industrial waste was deposited. This study fills this gap by presenting detailed analyses of total PTTE content and their geochemical forms using sequential BCR extraction in Technosols developed from various post-industrial parent materials, thereby extending the knowledge of trace element contamination, mobility and environmental risks in the unique environment of the Tatra Mountains. A study on Technosols developed on mining dumps near abandoned iron ore mines in Jaworzynka Valley in the Tatra Mountains stated that these soils did not contain high contents of As, Cd, Co, Cr, Cu, Ni, Pb and Zn [19]. However, results about the contents and geochemical forms of selected PTTE in other Technosols representing several important abandoned mining and smelting sites in the Tatra Mountains have not yet been presented.

The purpose of the present study was (1) to recognise the total contents of selected PTTE (Cu, Zn, Pb, Cd, Mo, Hg, As, Sb, Bi, Co, Ni, Ba, Sr, Ag, Au and Sn), radioactive elements (U and Th) and rare earth elements (REE) (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), as well as (2) to determine the geochemical forms of selected PTTE (Cu, Zn, Pb, Cd, As, Sb, Ba, Sr, Co, Ni, Mn and Cr) in soils from the Tatra Mountains using the BCR sequential extraction procedure. In addition to recognising total contents and determining the geochemical forms of selected PTTE, this study aims (3) to identify levels above limits (permissible contents) to evaluate the contamination status of Technosols by comparing measured PTTE concentrations against current Polish regulatory limits. This allowed for an assessment of the extent and potential environmental risks of trace element pollution in soils developed on historical mining and metallurgical wastes in the Tatra Mountains. The results allowed for a discussion on the degree of soil contamination, the origin of PTTE in soils and the potential mobility of PTTE in soils. Moreover, the results contribute to a more detailed recognition of the geochemical features of Technosols developed in the Tatra Mountains from different technogenic parent materials, Supplementary Data presented in previous studies [17–19].

2. Materials and Methods

2.1. Study Area and Object

The field research was conducted in 2020 in the Tatra Mountains, southern Poland, in historical mining and smelting areas. The study sites differed in the types of anthropogenic parent materials, including mining waste and metallurgical slags. These materials differed in the mineral composition of artefacts present in the soils, influencing soil properties [17]. Research was carried out in the following eight selected areas:

I. Huciańskie Banie (Mn and Fe ore mine)—Profiles 1 and 2.
II. Mouth of Kościeliska Valley (Fe ore mine)—Profile 3.
III. Kościeliska Valley near the Ornak tourist shelter (Cu and Ag ore prospection adit)—Profile 4.
IV. Pyszniańska Valley (Cu, Ag and Fe ore mine)—Profiles 5 and 6.
V. Żleb pod Banie (Pod Banie Couloir) at the Ornak ridge (Cu, Fe and Ag ore mine)—Profiles 7 and 8.
VI. Banisty Żleb (Banisty Couloir) at the Ornak ridge (Cu, Ag, Sb and Fe ore mine)—Profiles 9 and 10.
VII. Kościeliska Valley—an old steelwork (a former iron and non-ferrous metal smelting area at Stare Kościeliska)—Profiles 11 and 12.
VIII. The Kuźnice steelworks area (metal smelter)—Profile 13.

Soil profiles were located on surfaces of small heaps at adit outlets, as well as near collapsed shafts and historic smelters. The exact location was provided elsewhere [17].

Soil samples taken from each soil horizon distinguished in the field were analysed in the laboratory. Soil samples were first cleared of roots and organic debris, followed by air-drying at room temperature. The dried material was then passed through a 2 mm mesh sieve to separate the fine earth fraction (<2 mm). Standard pedological techniques, as described in established soil analysis references [50–52], were used to assess the physical and chemical properties of the fine earth. All studied soils were classified as Spolic Technosols or Coarsic Spolic Technosols [17] according to the WRB soil system [8].

2.2. Laboratory Analyses

2.2.1. Total Contents of PTTE

In the laboratory, living roots were removed from soil samples, and then the samples were dried at room temperature and sieved through a 2 mm sieve to obtain the fine earth fraction (<2 mm). Fine earth was used for all subsequent laboratory analyses. To determine the contents of PTTE (Cu, Zn, Pb, Cd, Mo, Hg, As, Sb, Bi, Co, Ni, Ba, Sr, Ag, Au and Sn), radioactive elements (U and Th) and rare earth elements (REE) (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), the fine earth soil samples were ground and mixed with $LiBO_2/Li_2B_4O_7$ flux. Crucibles were fused in a furnace. The cooled beads were dissolved in American Chemical Society (ACS)-grade nitric acid. Contents of elements were analysed using the inductively coupled plasma-mass spectroscopy (ICP-MS) method. Analyses were conducted at the Bureau Veritas Minerals Laboratories (BVML), Canada. The contents of Cu, Hg, Sb and Ag in Profiles 9 and 12 were higher than the maximum limit of detection of the method used. Therefore, these results were described adequately (e.g., >100) (Table S1).

2.2.2. BCR Sequential Extraction Analysis

Operationally defined chemical forms of selected PTTE (Cu, Zn, Pb, Cd, As, Sb, Ba, Sr, Co, Ni, Mn and Cr) were determined in soil samples using the BCR procedure [53–55]. This is a four-step sequential extraction protocol described in more detail in Table 1. In the laboratory, fine earth fractions (<2 mm) were used for BCR extraction. Samples were prepared by removing any remaining roots or organic debris and homogenised prior to fractionation.

Contents of elements in soil extracts gained during fractionation studies were determined using inductively coupled plasma-optical emission spectrometry (ICP–OES). Soil extracts were analysed in duplicate. Blanks were run in duplicate with each set of fractions. Analytical-grade reagents were used in the analyses. Analyses were performed at the

Department of Soil Science and Agricultural Chemistry, Facultad de Ciencias, Universidad de Granada, Spain.

Table 1. Fractions and reagents used in BCR sequential extraction [54,55].

Fraction	Reagent	Extraction Conditions	
		Time	Temperature
F1—exchangeable forms of an element	0.11 M·dm^{-3} CH_3COOH (pH = 7.0)	16 h	22 ± 5 °C
F2—forms of an element susceptible to reduction, including metal forms bound to Fe and Mn oxides	0.5 M·dm^{-3} $NH_2OH{\cdot}HCl$ (pH = 1.5)	16 h	22 ± 5 °C
F3—oxidisable forms of an element, including metal forms associated with organic matter and sulphides	30% H_2O_2, next 1.0 M·dm^{-3} CH_3COONH_4 (pH = 2.0)	1 h 22 ± 5 °C, 1 h 85 ± 2 °C, 1 h 85 ± 5 °C, 16 h 22 ± 5 °C	
F4—residual forms of an element	Aqua regia (HNO_3 + HCl 3:1)	Appropriate mineralisation program Ethos UP apparatus	

2.3. Statistical Analysis

The distribution of the results was checked for normality using the Shapiro–Wilk test. Since the assumption of normality was not consistently met, the non-parametric Spearman's rank correlation was applied to evaluate the strength and direction of the relationships between the PTTE concentrations bound in operationally defined fractions and soil properties (pH, carbonate content and total organic carbon (TOC)). The correlation coefficients (ρ) and corresponding *p*-values were calculated, with the statistical significance level at $p < 0.05$. Statistical analysis was performed in Statistica^{TM} 13.3 (Tibco Software Inc., Palo Alto, CA, USA).

3. Results

3.1. Soil Properties

The studied Technosols were divided into three distinct groups differing in the nature of the anthropogenic parent material and soil properties [17]. A summary of the results showing the soil characteristics is presented below and in Table S2.

Group I Technosols (Profiles 1–3) were carbonate-rich mining waste soils. They displayed neutral to alkaline pH_{H2O} (7.2–8.1; with the exception of P3, horizons Oe—5.7, O/C—6.8) due to high carbonate content (9.6%–31.2% $CaCO_3$ eq.) (Table S2). These soils, derived from Fe- and Mn-ore and carbonate-bearing mining waste, were strongly buffered by carbonates. The total organic carbon (TOC) content was very high in organic horizons (43% on average; with the exception of P3, horizons O/C—24%) and lower in mineral horizons (4% on average) (Table S2), following typical soil depth-dependent trends [17].

Group II Technosols (Profiles 5–10) were soils derived from aluminosilicate mining waste near abandoned polymetallic ores. They were acidic soils (pH_{H2O} 3.6–6.0) (Table S2), reflecting their origin from non-carbonate igneous (granite) and metamorphic (gneiss) rocks. Surface layers under coniferous vegetation (e.g., Pyszniańska Valley, Banisty Couloir and Pod Banie Couloir) exhibited the lowest pH (pH_{H20} 4.0 on average). The TOC content averaged 2% (in mineral horizons), with the highest accumulation in organic horizons (39% on average) (Table S2) [17].

Group III Technosols (Profiles 11–13) were soils containing metallurgical waste. They exhibited variable pH_{H2O} (5.6–8.6) and low carbonate content (on average 3% $CaCO_3$ eq.) (Table S2). Profiles 11 and 12 had lower pH levels than Profile 13. The TOC contents

throughout the soil profiles were notably higher (7% on average in mineral horizons; 43% on average in organic horizons) than in other soils, peaking at 15% in Profile 12 (2C horizon) (Table S2) due to the occurrence of charcoal-rich anthropogenic materials [17].

Profile 4 exhibited intermediate properties between Group I and Group II, with pH (Table S2) influenced by mixed carbonate and aluminosilicate parent materials [17].

3.2. Total Contents of PTTE in the Studied Soils

In Group I Technosols (Profiles 1–3), derived from carbonate-bearing mining waste near abandoned Fe and Mn ore mines, the most notable feature was elevated contents of Co (up to 205 mg·kg^{-1}) and Ni (up to 431 mg·kg^{-1}) (Figure 1; Table S1). This feature was typical for Profiles 1 and 2. These values far exceeded those found in Groups II and III, where the Ni and Co contents reached up to 74 mg·kg^{-1} and 79 mg·kg^{-1} (Figure 1; Table S1), respectively. These soils contained relatively low contents of other PTTE (e.g., Cu, Hg, Sb, Cr, Bi and Ag), although Zn, Mo and Sr showed elevated contents compared to soils in other studied locations.

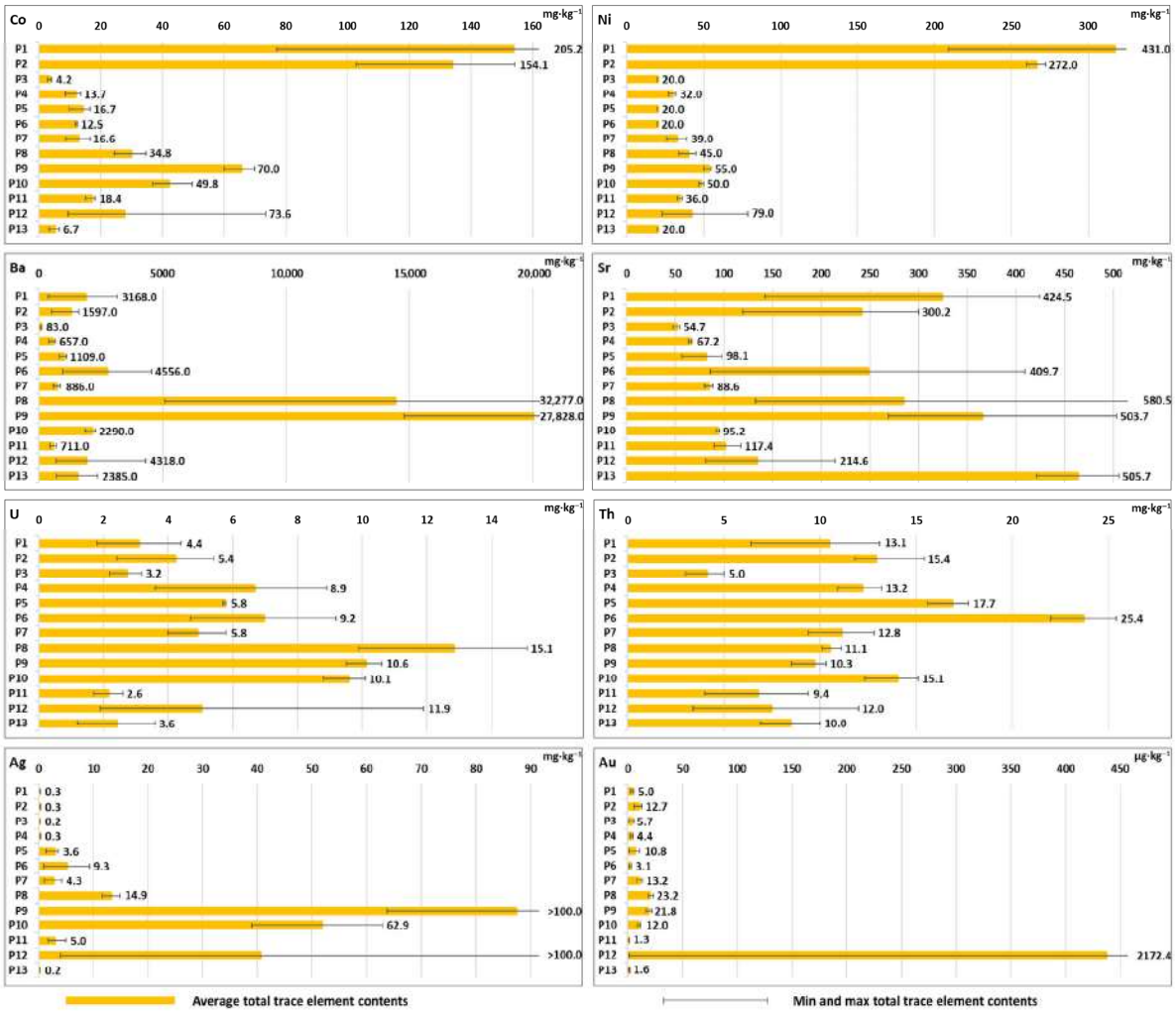


Figure 1. Average (marked as orange bars), minimal and maximal (marked as black lines; numbers near the bar show maximum concentration of the element) total concentrations of Co, Ni, Ba, Sr, U, Th, Ag and Au in the studied soil profiles (P1–P13). Total concentrations of elements in individual soil horizons are shown in Table S1 (Supplementary Materials).

Group II Technosols (Profiles 5–10), derived from aluminosilicate mining waste near abandoned polymetallic ores, showed very high variability in PTTE contents. Profile 8

from Pod Banie Couloir contained particularly high amounts of Mo (up to 20 mg·kg^{-1}), Ba (up to 32,277 mg·kg^{-1}), Sr (up to 581 mg·kg^{-1}), U (up to 15 mg·kg^{-1}) and Au (up to 23 µg·kg^{-1}) (Figures 1 and 2; Table S1). Profile 9 from Banisty Couloir showed significant enrichment in many PTTE, including Cu (up to 1666 mg·kg^{-1}), Zn (up to 159 mg·kg^{-1}), Hg (up to 37 mg·kg^{-1}), As (up to 347 mg·kg^{-1}), Sb (up to 1263 mg·kg^{-1}), Bi (up to 21 mg·kg^{-1}), Co (up to 70 mg·kg^{-1}), Ba (up to 27,828 mg·kg^{-1}), Sr (up to 504 mg·kg^{-1}), U (up to 11 mg·kg^{-1}), Th (up to 10 mg·kg^{-1}), Ag (>100 mg·kg^{-1}) and Au (up to 22 µg·kg^{-1}) (Figures 1 and 2, Table S1). Profile 6 from Pyszniańska Valley contained the highest Th content (up to 25 mg·kg^{-1}) in this group, while Profile 10, located at the same site as Profile 9, contained the same elements but in lower concentrations than Profile 9 (with the exception of Th—15 mg·kg^{-1}) (Figure 1; Table S1).

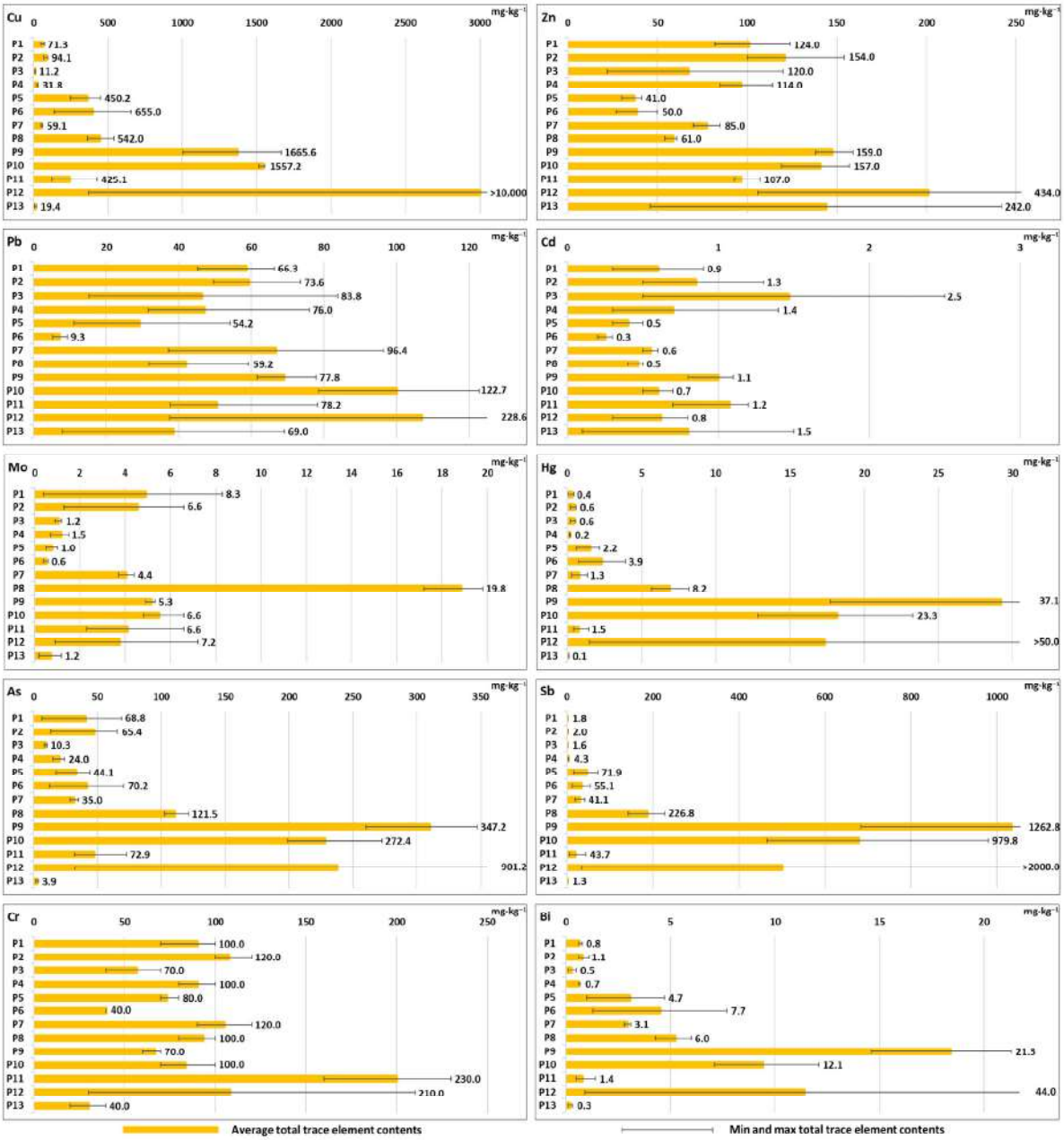


Figure 2. Average (marked as orange bars), minimal and maximal (marked as black lines; numbers near the bar show maximum concentration of the element) total concentrations of Cu, Zn, Pb, Cd, Mo, Hg, As, Sb, Cr and Bi in the studied soil profiles (P1–P13). Total concentrations of elements in individual soil horizons are shown in Table S1 (Supplementary Materials).

The most complex contamination patterns appeared in Group III Technosols (Profiles 11–13), representing soils in old smelting areas. The concentrations of all studied elements in Profile 11 were typically low in comparison with the other soils; however, Cr reached its maximum concentration in this profile, up to 230 mg·kg^{-1}. Profile 12 showed particularly significant PTTE variation between horizons, with high total contents of As, Cu, Sb and Ba throughout the soil profile. The 3C horizon in Profile 12 contained extreme concentrations of Cu (>10,000 mg·kg^{-1}), Zn (434 mg·kg^{-1}), Hg (>50 mg·kg^{-1}), As (901 mg·kg^{-1}), Sb (>2000 mg·kg^{-1}), Bi (44 mg·kg^{-1}), Ag (>100 mg·kg^{-1}) and Au (2172 µg·kg^{-1}) (Figures 1 and 2; Table S1). However, the 3C horizon in Profile 12 constituted a layer of ore-bearing rocks (not metallurgical waste) preserved within the soil profile. Profile 13 showed lower contents of the aforementioned PTTE except for Sr (up to 506 mg·kg^{-1}), which showed one of the highest contents of that element among the studied soils (Figure 1; Table S1).

Profile 4 showed moderate concentrations of PTTE. Zinc reached up to 114 mg·kg^{-1}, Cr up to 100 mg·kg^{-1}, Pb up to 76 mg·kg^{-1}, As up to 24 mg·kg^{-1}, Co up to about 14 mg·kg^{-1} and Ni up to 32 mg·kg^{-1}. Barium (Ba) showed higher levels, up to 657 mg·kg^{-1}, while Sr reached about 67 mg·kg^{-1}. Uranium and Th were present up to about 9 mg·kg^{-1} and 13 mg·kg^{-1}, respectively. Profile 4 contained relatively low contents of other PTTE (e.g., Cu, Cd, Mo, Hg, Sb, Bi, Ag and Au) (Figures 1 and 2; Table S1).

3.3. Total Contents of Rare Earth Elements (REE) in the Studied Soils

The studied soils showed distinct REE (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) distribution patterns across the three Technosol groups (Table 2), reflecting differences in parent material composition.

Group I Technosols (Profiles 1–3), in general, contained the highest contents of REE in comparison with the other soils (from 61–786 mg·kg^{-1}) (Table 2). This was particularly true for Profiles 1 and 2, where the most common REE were Ce (107–293 mg·kg^{-1}), La (50–116 mg·kg^{-1}), Nd (45–120 mg·kg^{-1}), Y (33–113 mg·kg^{-1}), Sm (8.5–23 mg·kg^{-1}), Gd (7.6–25 mg·kg^{-1}) and Dy (6–19 mg·kg^{-1}). Profile 3 contained the lowest total REE concentrations (61–126 mg·kg^{-1}), as it was developed in a mining area other than the site where Profiles 1 and 2 were located.

Total REE contents (61–346 mg·kg^{-1}) in Group II Technosols (Profiles 5–10) were lower than in Group I, with the highest values in Profile 6 (C horizon) (Table 2). Soils of that group showed relative enrichment in Ce (61–127 mg·kg^{-1}), La (31–61 mg·kg^{-1}), Nd (28–59 mg·kg^{-1}) and Y (20–45 mg·kg^{-1}).

Group III Technosols in historical smelting areas (Profiles 11–13) displayed the lowest total REE contents (59–237 mg·kg^{-1}). Profile 13 (AC horizon: 237 mg·kg^{-1}) contained the highest contents of REE in that group. Cerium (19–89 mg·kg^{-1}) and La (11–36 mg·kg^{-1}) were predominant REE, but their contents were significantly lower than in Groups I and II Technosols. Profile 12 showed irregular REE distribution, with an abrupt decrease in total contents of REE in the 2C and 3C horizons (Table 2).

The total REE contents (159–214 mg·kg^{-1}) (Table 2) in Profile 4 were relatively low in comparison with the other soils studied.

Table 2. Concentrations of rare earth elements (REE) in the studied Technosols.

Soil Profile	Horizon	Depth (cm)	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sum of REE	
											mg·kg^{-1}									%
P1	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	AC1	1–5	9	62.1	70.4	213.7	17.25	71.3	14.12	3.18	15.12	2.09	11.72	2.23	5.95	0.78	4.37	0.65	504	0.05
	AC2	5–15	12	61.2	85.3	286.7	21.16	87.5	16.56	3.48	16.29	2.25	12.05	2.28	5.98	0.74	4.29	0.62	618	0.06
	C	15–35	15	65.1	83.4	255.8	21.80	90.2	16.95	3.70	16.98	2.34	12.40	2.30	5.95	0.77	4.30	0.62	598	0.06
	2C	35–60	17	33.3	49.6	106.6	11.65	45.4	8.51	1.76	7.58	1.08	6.11	1.17	3.28	0.44	2.82	0.44	297	0.03
P2	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	AC1	1–25	16	87.7	93.8	241.1	23.76	98.2	19.14	4.13	20.03	2.76	15.23	2.88	7.46	0.92	5.27	0.78	639	0.06
	AC2	25–45	17	113.2	115.8	292.5	28.7	120.1	23.18	5.19	24.94	3.47	19.02	3.75	9.77	1.21	6.71	0.99	786	0.08
	AC3	45–65	17	101.7	108.9	273.9	26.16	109.5	21.28	4.71	22.73	3.12	17.91	3.37	8.82	1.09	6.27	0.89	727	0.07
	2C	65–90	20	69.6	82.5	148.7	19.64	81.0	15.13	3.24	14.23	1.94	11.12	2.11	5.87	0.77	4.64	0.73	481	0.05
P3	Oe	0–6	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	O/C	6–25	3	8.4	10.4	20.0	2.36	9.5	1.68	0.33	1.63	0.23	1.34	0.26	0.78	0.10	0.64	0.09	61	0.01
	AC	25–40	4	13.2	16.4	29.7	3.50	13.6	2.60	0.49	2.39	0.37	2.09	0.45	1.31	0.18	1.10	0.18	92	0.01
	BC	40–60	4	28.8	17.5	36.0	4.27	15.9	3.33	0.64	3.74	0.67	4.34	0.98	2.64	0.38	2.37	0.36	126	0.01
P4	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–13	9	20.5	27.3	53.7	6.27	23.4	4.30	0.75	4.01	0.63	3.90	0.76	2.14	0.32	1.99	0.30	159	0.02
	C1	13–35	13	27.3	35.4	72.8	8.30	31.0	6.04	1.35	6.14	0.89	4.97	0.97	2.73	0.36	2.34	0.36	214	0.02
	C2	35–60	13	27.0	35.4	73.2	8.25	30.7	6.25	1.36	6.01	0.89	5.06	0.96	2.73	0.40	2.47	0.37	214	0.02
P5	Oe	0–3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Oa	3–10	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	A	10–15	11	43.7	40.3	82.2	9.97	38.0	7.52	1.24	6.96	1.17	7.14	1.47	4.46	0.61	3.73	0.54	260	0.03
	Bw	15–20	13	36.7	39.5	83.8	10.09	38.4	8.26	1.48	7.96	1.19	6.85	1.30	3.68	0.50	3.07	0.45	256	0.03
	C	20–45	14	45.7	36.1	75.5	9.43	36.3	8.37	1.49	8.34	1.38	8.12	1.68	4.78	0.63	3.97	0.56	256	0.03
P6	Oe	0–2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	Oa	2–10	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	ABw	10–20	10	32.4	55.4	115.6	14.12	52.8	9.74	1.44	8.09	1.16	6.38	1.13	3.16	0.42	2.62	0.37	315	0.03
	C	20–65	10	35.0	61.4	127.3	15.52	58.9	10.99	1.74	9.03	1.21	6.51	1.27	3.39	0.44	2.83	0.43	346	0.04
P7	Oe	0–2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	AC	2–15	10	20.2	32.1	63.8	7.68	28.3	5.42	0.90	4.51	0.63	3.74	0.69	1.99	0.27	1.82	0.27	182	0.02
	C	15–50	13	27.1	39.5	83.8	9.96	38.4	7.69	1.58	6.74	0.94	5.30	0.96	2.73	0.40	2.45	0.36	241	0.02

Table 2. *Cont.*

Soil Profile	Horizon	Depth (cm)	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sum of REE	
											mg·kg^{-1}									%
P8	Oe	0–4	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	AC	4–15	13	25.0	32.9	63.0	7.48	28.0	5.40	1.24	5.09	0.74	4.79	0.85	2.52	0.34	2.14	0.32	193	0.02
	C1	15–35	13	30.2	32.6	64.8	7.54	29.5	6.51	1.67	6.68	1.02	5.81	1.13	3.14	0.43	2.64	0.40	207	0.02
	C2	35–55	16	29.2	32.2	64.4	7.72	29.8	6.59	1.76	6.43	0.96	5.65	1.01	2.90	0.39	2.40	0.38	208	0.02
P9	Oi	0–2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	AC	2–10	10	21.6	31.3	61.2	7.18	27.9	5.57	1.15	4.55	0.64	3.99	0.77	2.28	0.31	2.01	0.32	181	0.02
	C1	10–40	12	28.8	35.6	70.8	8.41	33.0	6.66	1.50	5.96	0.88	5.34	1.00	2.81	0.40	2.61	0.39	216	0.02
	C2	40–80	12	29.6	35.1	69.8	8.28	33.0	6.50	1.53	6.33	0.88	5.35	1.02	2.95	0.44	2.69	0.40	216	0.02
P10	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	AC	1–10	16	41.1	39.9	81.9	10.06	39.3	8.37	1.80	7.67	1.17	7.08	1.41	3.93	0.56	3.51	0.53	264	0.03
	C1	10–50	15	33.4	38.5	78.2	9.70	38.0	7.65	1.66	6.96	1.01	5.92	1.15	3.33	0.47	2.95	0.45	244	0.02
	C2	50–70	13	29.8	36.8	74.6	9.08	34.7	6.99	1.37	6.18	0.90	5.33	1.03	2.96	0.41	2.73	0.41	226	0.02
P11	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–15	8	18.7	26.6	50.9	5.97	22.5	4.15	0.81	3.60	0.55	3.33	0.67	1.96	0.27	1.84	0.28	150	0.02
	C1	15–30	9	21.5	31.7	61.9	7.45	28.0	5.21	1.03	4.65	0.67	4.08	0.77	2.16	0.29	2.00	0.31	181	0.02
	C2	30–45	6	13.1	19.5	36.7	4.44	17.0	3.13	0.60	2.75	0.38	2.54	0.47	1.37	0.17	1.30	0.19	110	0.01
	C3	45–60	5	9.8	13.6	26.8	3.25	12.4	2.21	0.47	2.03	0.28	1.59	0.35	0.97	0.13	0.84	0.14	80	0.01
P12	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–20	7	14.8	23.6	45.8	5.54	20.5	3.70	0.68	3.23	0.45	2.60	0.50	1.48	0.20	1.33	0.20	132	0.01
	C1	20–28	9	20.1	29.2	59.2	6.92	25.2	4.45	0.81	3.76	0.57	3.36	0.69	1.90	0.28	1.89	0.28	168	0.02
	2C	28–50	3	7.9	10.8	19.2	2.31	9.0	1.78	0.24	1.57	0.22	1.30	0.24	0.66	0.10	0.67	0.09	59	0.01
	3C	50–60	5	11.4	13.6	26.7	3.11	12.4	2.60	0.96	2.75	0.38	2.09	0.35	0.99	0.14	0.98	0.13	84	0.01
	4C	60–75	9	24.6	34	67.7	8.10	29.4	5.52	0.86	4.73	0.71	4.22	0.86	2.63	0.36	2.33	0.36	195	0.02
P13	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
	AC	1–15	15	28.5	35.9	89.0	8.90	33.2	6.55	1.54	5.82	0.86	5.05	0.95	2.82	0.39	2.38	0.36	237	0.02
	2C	15–25	5	11.1	24.7	48.3	5.76	22.0	3.67	0.84	2.99	0.38	2.02	0.36	0.95	0.13	0.84	0.12	129	0.01

Explanation: – not analysed.

3.4. Geochemical Forms of Selected PTTE in the Studied Soils Based on BCR Sequential Extraction

Geochemical forms of Cu, Zn, Pb, Cd, As, Sb, Ba, Sr, Co, Ni, Mn and Cr in the investigated Technosols varied between soil profiles as well as between soil horizons within each soil profile, showing high heterogeneity of soil substrates (Figures 3–5).

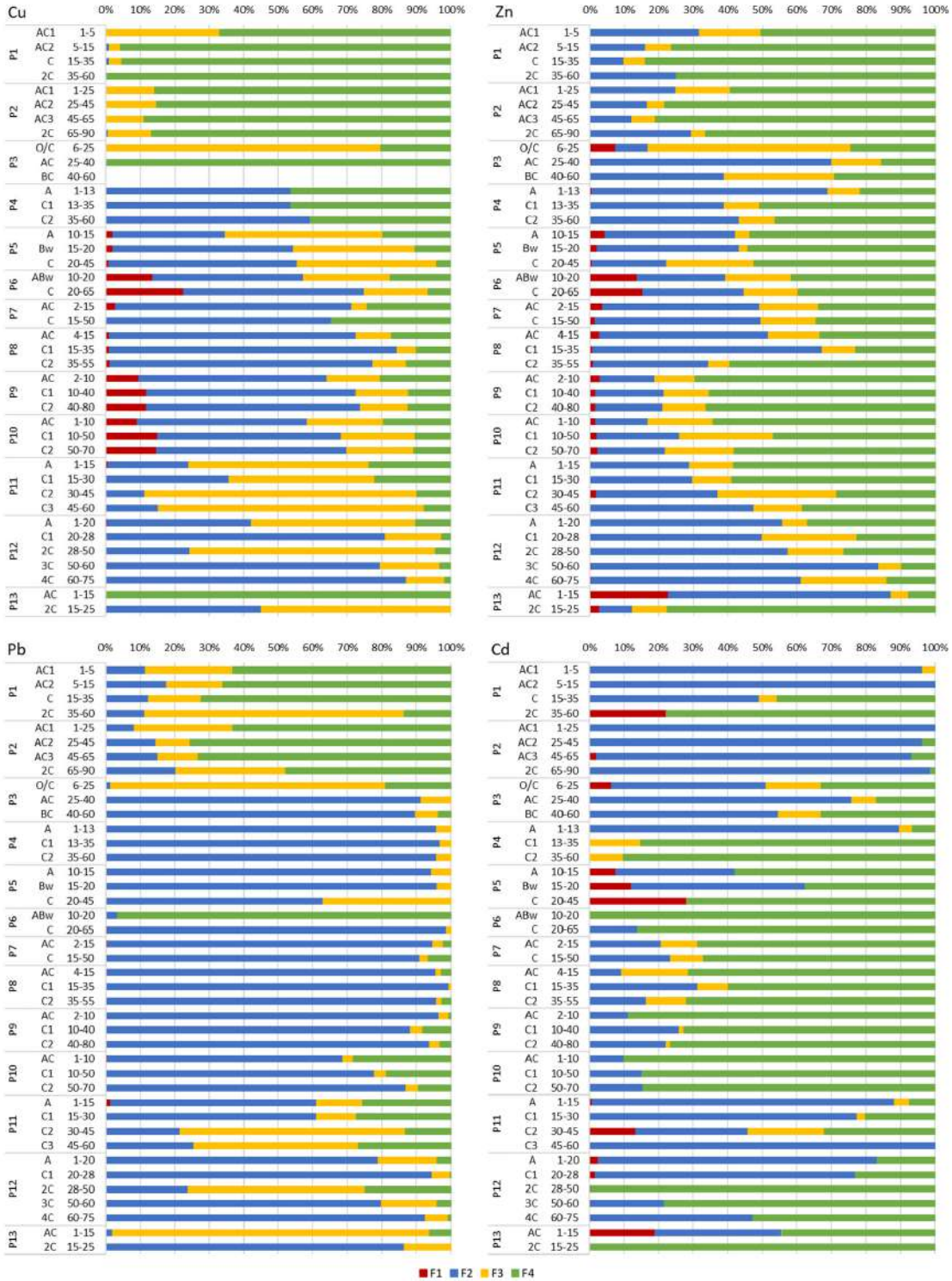


Figure 3. Chemical forms of Cu, Zn, Pb and Cd in the studied soils based on BCR sequential extraction. Operational definitions of fractions: F1—exchangeable, soluble in acidic medium; F2—susceptible to reduction, including element forms bound to Fe and Mn oxides; F3—oxidisable, including element forms associated with organic matter and sulphides; F4—residual. Detailed descriptions of fractions (from F1 to F4) are presented in Table 1.

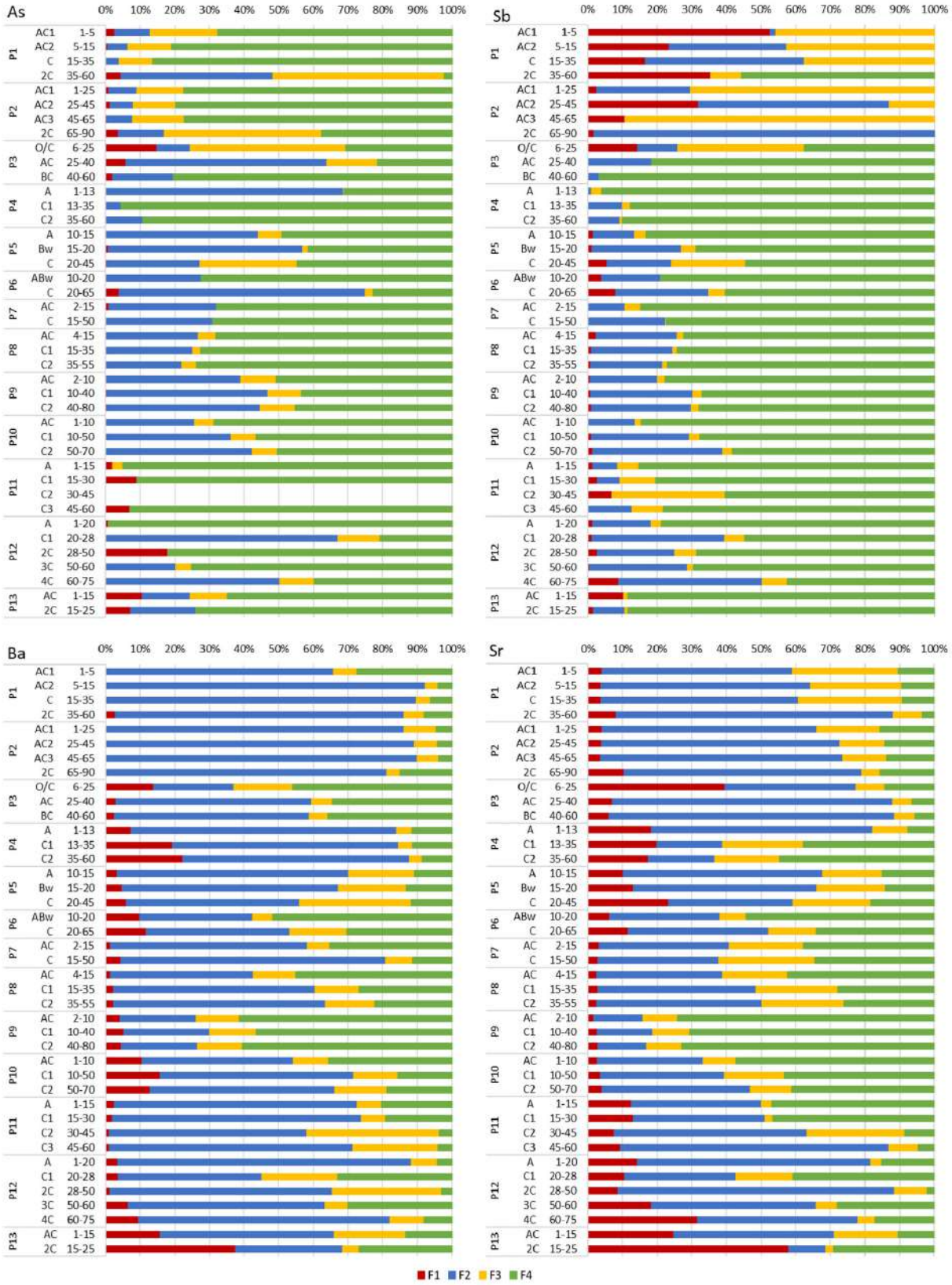


Figure 4. Chemical forms of As, Sb, Ba and Sr in the studied soils based on BCR sequential extraction. Operational definitions of fractions: F1—exchangeable, soluble in acidic medium; F2—susceptible to reduction, including element forms bound to Fe and Mn oxides; F3–oxidisable, including element forms associated with organic matter and sulphides; F4—residual. Detailed descriptions of fractions (from F1 to F4) are presented in Table 1.

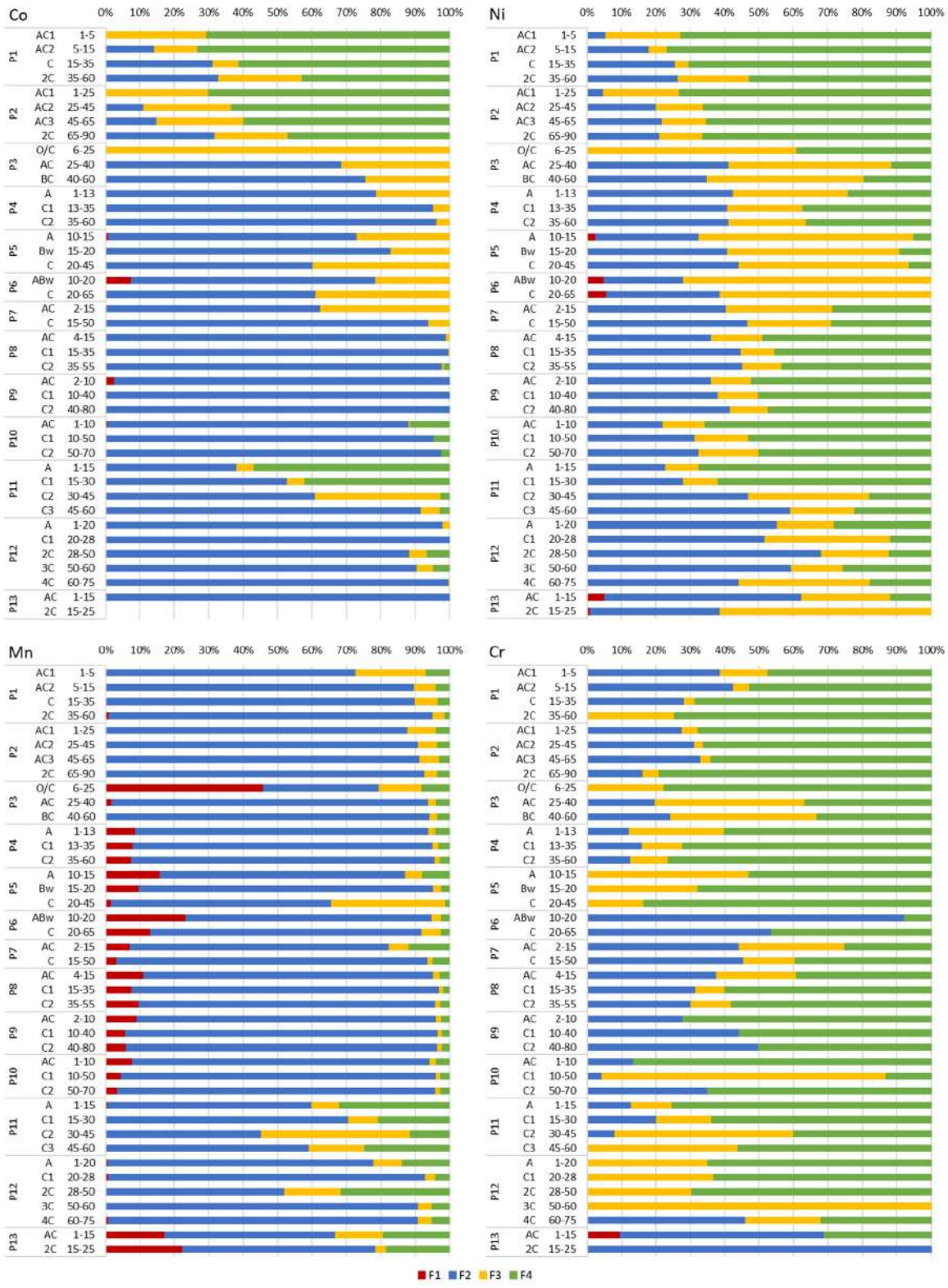


Figure 5. Chemical forms of Co, Ni, Mn and Cr in the studied soils based on BCR sequential extraction. Operational definitions of fractions: F1—exchangeable, soluble in acidic medium; F2—susceptible to reduction, including element forms bound to Fe and Mn oxides; F3—oxidisable, including element forms associated with organic matter and sulphides; F4—residual. Detailed descriptions of fractions (from F1 to F4) are presented in Table 1.

In Group I Technosols (Profiles 1–3), Cu dominated the residual fraction (F4, 67%–100%), except for Profile 3 (P3) topsoil (F3—oxidisable forms, 80%) (Figure 3). Zinc

prevailed in F4 (50%–84%) in Profile 1 (P1) and Profile 2 (P2). Profile 3 contained Zn in F3 (59%) in the topsoil and F2 (reducible forms) (up to 69%) in the subsoil. Lead dominated F4 (up to 75%), except for P3 (F3, 80%) and P1 (F3, 75%). Profile 3 subsoil had Pb in F2 (up to 91%). Cadmium occurred mainly in F2 (45%–100%), except for the deepest horizon of P1 (F4, 78%). Arsenic dominated F4 (67%–86%), with exceptions (F3) in the deepest horizons of P1–P2 and (F2) the AC horizon of P3 (Figure 4). A significant share of As in P3 topsoil was present in F1. Antimony showed high diversity of forms and occurred in F4 (up to 97% in P3), F3 (up to 89% in P2), F2 (up to 98% in P2) and F1 (exchangeable forms) (up to 53% in P1). Barium prevailed in F2, except for P3 topsoil (F4, 46%). Strontium dominated F2, with a slightly higher share in F1 in P3 topsoil (40%). Cobalt dominated F4 (43%–73%) in P1 and P2 (Figure 5). Profile 3 contained Co in F3 (100%) in topsoil and F2 (69%–76%) in subsoil. Nickel dominated F4 (53%–77%) in P1–P2. Profile 3 subsoil showed Ni in F3 (46%–61%). Cobalt and Ni exhibited similar behaviours in P1 and P2 throughout the soil profiles. Manganese dominated F2 (73%–94%); however, a high share of F1 (46%) was typical of P3 topsoil. Chromium prevailed in F4 (47%–79%), except for P3 subsoil (F3, up to 44%) (Figure 5).

In Group II Technosols (Profiles 5–10), the residual fraction (F4) was dominated by Zn (up to 69%), Cd (up to 100%), As (up to 74%) and Sb (up to 85%), though reducible forms (F2) were significant for Cu (up to 83%), Pb (up to 99%), Co (up to 100%), Mn (up to 93) and Ba (up to 76%) (Figures 3–5). Nickel was present in F2 (up to 47%), F3 (up to 72%) and F4 (up to 66%). Antimony occurred in F2 (up to 57%) and in F4 (up to 74%). Chromium was bound mostly in F2 (up to 92%) and in F4 (up to 86%) (Figures 3–5). Exceptions included Cu in F3 (46%) in topsoil of P5; Zn in F2 (46%–66%) in the horizons AC and C of P7 and horizons AC and C1 of P8; Pb in F4 (97%) in the ABw horizon of P6; Cd in F2 (50%) in the Bw horizon of P5; As in F2 (56%) in the Bw horizon of P5, (71%) in the C horizon of P6 and (46%) in the C1 horizon of P9; Ba in F4 (52%) in the ABw horizon of P6, (45%) in the AC horizon of P8 and (up to 61%) in P9; and Cr in F3 (83%) in the C1 horizon of P10 (Figures 3–5).

Group III Technosols (Profiles 11–13) showed complex element distributions. Profile 11 showed Cu in F3 (up to 79%) (Figure 3). In P12, Cu occurred in F2 (81%–87%) in the C1, 3C and 4C horizons and in F3 in the A (48%) and 2C (71%) horizons. Zinc dominated F2 (up to 83%), except for F4 (up to 78%) in AC and C1 of P11 and in 2C of P13 (78%). Lead occurred mostly in F2 (up to 94% in P12) and F3 (up to 92% in P13). Cadmium dominated F2 (up to 100% in P11 and in the subsoil horizons of P12) and F4 (up to 100% in P13 and deeper horizons of P12). Arsenic dominated F4, except for the C1 and 4C horizons of P12 (F2, 67% and 50%) (Figure 4). Antimony dominated F4 (42%–88%). Barium occurred mostly in F2, except for the subsoil of P13 (F1, 38%). Strontium prevailed in F2, except for the subsoil of P13 (F1, 58%), as well as for the A and C1 horizons of P11 and the C1 horizon of P12 (F4). Barium and Sr showed similar trends in P11–P13. Cobalt, Mn and Ni dominated F2, except for a few soil horizons (Figure 5). Chromium in P11 and P12 occurred mostly in F4, and in P13 mostly in F2, except for the C2 horizon of P11 (F3) and the 3C (F3) and 4C (F2) horizons of P12.

Profile 4 showed varied geochemical forms of PTTE. Copper and Zn were mainly present in F2 (up to 68%) and F4 (up to 51%) (Figure 3). Lead, Co and Mn were found largely in F2 (up to 97%) (Figures 3 and 5). Cadmium and As occurred significantly in F2 (up to 90%) in the topsoil and F4 (up to 95%) in the subsoil. Antimony was mainly present in F4 (88%–96%). Barium and Sr primarily occurred in F2 (up to 77%) and up to 22% in F1 (Figures 3 and 4). Nickel and Cr were mostly in F2 (up to 43%) and F4 (up to 76%) (Figure 5).

4. Discussion

4.1. Contamination of Technosols Based on the Total Contents of PTTE Against Polish Regulations and by Comparison with Other Soils in the Tatra Mountains

The PTTE contents in the analysed soils were evaluated against Poland's regulatory standards, which serve as the benchmark for assessing land surface contamination [56]. In the case of Poland, national soil regulations are influenced by European Union directives [57]. These regulations establish permissible contents of selected metal(loid)s (i.e., As, Ba, Cr, Sn, Zn, Cd, Co, Cu, Mo, Ni, Pb and Hg) in the soil for various land use categories, differentiating permissible contents for two depths (0–25 cm and below 25 cm). Polish law classifies land into four groups (I–IV): (1) land group I includes urban and developed areas inhabited by human; (2) land group II includes agricultural lands (arable fields, orchards, meadows), but also national parks and natural reserves; (3) land group III includes forested and shrub-covered regions; and (4) land group IV includes industrial zones, transportation corridors, production facilities, storage areas, technical infrastructure sites and mining districts. Additionally, land group II is further divided into three subgroups (II-1, II-2 and II-3) based on specific soil characteristics such as texture, pH and organic carbon content. For soils below 25 cm, permissible trace element levels are dependent on water permeability, with a threshold value of 1×10^{-7} m·s^{-1} [56].

The results obtained in this study were compared with the permissible contents of metal(loid) standards in soil for proper subgroups in land group II (Table S1) [56]. Permissible levels of elements were exceeded for the following metal(loid)s: Cu (Profiles P5, P6, P8–P12), Zn (P12—3C horizon), Pb (P10, P12), Mo (P8), Hg (P5, P6, P8–P10, P12), As (P1, P2, P4–P12), Co (P1, P2, P8–P10, P12—3C horizon), Ni (P1, P2) and Ba (P1, P2, P4–P13) (Table S1). The copper content in Technosols exceeded permissible limits by more than 16 times (in Profile P9), and Pb and Mo by 1.2 and 2 times, respectively. Permissible values for Hg were exceeded by 18 times and for As by 34 times in these soils. Cobalt and Ni reached values 6 and 4 times higher, respectively, than those specified in Polish regulations. Barium reached values 160 times higher than the threshold values. The 3C horizon of Profile 12, which is most likely a layer containing remnants of ore material containing high concentrations of all studied elements, exceeded permissible contents of Cu (66 times), Zn (1.4 times), Pb (1.7 times), Hg (16 times), As (45 times), Co (2.5 times) and Ba (7.5 times). By contrast, the concentrations of Cr, Cd and Sn in all studied soils did not exceed permissible limits.

The elevated contents of PTTE such as Cu, Zn, Pb, Mo, Hg, As, Co, Ni and Ba in the studied Technosols derived from mining waste and old smelting areas often exceeded concentrations reported for native soils in the Tatra Mountains. For instance, Cu, Zn, Pb and Ni contents in Group II Technosols (up to 1666 mg·kg^{-1} of Cu, 159 mg·kg^{-1} of Zn, 123 mg·kg^{-1} of Pb and 55 mg·kg^{-1} of Ni) were significantly higher than those detected in a study of natural mountain podzols of the Tatra Mountains [38], where authors reported much lower trace element contents (up to 36 mg·kg^{-1} of Cu, 89 mg·kg^{-1} of Zn, 50 mg·kg^{-1} of Pb and 27 mg·kg^{-1} of Ni) attributed to natural lithology and podzolisation processes. Lower average contents of Cu (up to 13 mg·kg^{-1}), Zn (up to 92 mg·kg^{-1}), Pb (up to 67 mg·kg^{-1}) and Ni (up to 16 mg·kg^{-1}), in comparison to the studied Technosols, were also recorded in soils presented in another study [47]. Similarly, lower average contents of heavy metals such as Cu (up to 15 mg·kg^{-1}), Zn (up to 125 mg·kg^{-1}) and Ni (up to 16 mg·kg^{-1}) were recorded in soils near Lake Morskie Oko and Kasprowy Wierch, with pollution indices generally suggesting low to moderate contamination mostly influenced by long-range atmospheric deposition rather than local mineralisation or metallurgical activities [31]. Although higher concentrations of Zn, Pb and Cd in non-forest soils of Tatra National Park than in the analysed Technosols were reported [48], their spatial distribution was strongly controlled by natural factors like parent

rock composition, with less influence from anthropogenic contamination. It can be concluded that the PTTE levels in the studied Technosols markedly exceed concentrations reported in the aforementioned studies, reflecting local anthropogenic pollution from mining and smelting activities, whereas the trace metal contents in undisturbed mountain soils of the Tatra region generally remain within natural or slightly elevated ranges associated with geological and atmospheric factors [31,48].

4.2. Origin of PTTE in the Studied Technosols

The analysed Technosols developed from three different types of mining and industrial wastes. Therefore, the origin of the high contents of PTTE in the investigated Technosols is complex and depends on the nature of anthropogenic parent material.

Group I Technosols (Profiles 1–3), in particular Profiles 1 and 2, contained high concentrations of Ni (up to 431 mg·kg^{-1}) and Co (up to 205 mg·kg^{-1}) (Table S1). Soils around the world contain Ni over a very wide range, but the average levels reported for different countries are in the relatively low range of 13–37 mg·kg^{-1} [58]. Nickel content is the lowest in sandy and organic soils and highest in heavy loamy and calcareous soils [58]. The world average Co content in soils was estimated at 10 mg·kg^{-1} [59]. High contents of Ni and Co in Profiles 1 and 2 from the Tatra Mountains were most likely related to high concentrations in the parent material, i.e., mining waste containing remnants of Fe and Mn ores. Nickel and Co are frequently enriched in Fe-Mn ores due to adsorption and incorporation mechanisms in Fe and Mn oxide minerals [60]. Moreover, there were also high contents of Ba (up to 3168 mg·kg^{-1}) in Group I Technosols. Barium is typically found in low concentration in soils. High levels of Ba in soils can come from industrial activities, such as mining [58]. Barium is commonly associated with carbonate rocks [61], as it is often incorporated into carbonate minerals or is found adsorbed on carbonate phases in marine and sedimentary environments [62]. Studies have shown that Ba concentrations can vary in carbonate rocks due to their association with carbonate mineral phases such as calcite and aragonite [63]. Additionally, Ba can be present in barite ($BaSO_4$), which can form in marine sedimentary settings, often associated with carbonate deposits [64].

Group II Technosols (Profiles 5–10), developed from aluminosilicate igneous and metamorphic rocks containing remnants of polymetallic ores, had very high Cu (up to 1666 mg·kg^{-1} in Profile 9) and As (up to 347 mg·kg^{-1} in Profile 9) contents. In the soils of European Union countries, average Cu contents range from 5 to 50 mg·kg^{-1} [59]. The average As content in soils generally ranges from about 1 to 15 mg·kg^{-1}, depending on the region, with natural background levels typically below 10 mg·kg^{-1} [59]. High Cu and As contents are typical of polymetallic ore-related mining waste [28,65–67], where these elements are primarily linked to the sulphide mineralisation in rocks [68,69]. Similar mineralogical controls were documented on metal occurrence in sulphide-rich Technosols developed from mining waste [9,67]. Metal(loid)-rich minerals in the area of Ornak ridge, where historical Cu-Ag-Sb-Fe ore mining was conducted, are, for example, chalcopyrite ($CuFeS_2$)—a primary copper-bearing sulphide, pyrite (FeS_2) often associated with arsenic as an impurity—as well as arsenopyrite (FeAsS) and enargite (Cu_3AsS_4), which are arsenic-rich minerals [68]. High contents of Hg (up to 37 mg·kg^{-1}) were found in Profiles P8–P10, representing Group II Technosols. The presence of Hg is linked to remnants of polymetallic ore minerals scattered in aluminosilicate igneous and metamorphic rocks. Mercury in the rocks constituting the parent materials of the studied soils was most likely accumulated due to hydrothermal mineralisation processes occurring in rocks during ore formation [68]. Typically, Hg is present primarily in sulphide minerals that form in hydrothermal veins [70]. Cinnabar (HgS) is the major mercury mineral, but Hg is also found as a trace element in other sulphide minerals, including sphalerite (ZnS), chalcopyrite and tetrahedrite, within hydrothermal mineral deposits [71]. Group

II Technosols contained the highest Ba content (up to 32,277 mg·kg^{-1}) among the studied Technosols. This was primarily due to the presence of barite ($BaSO_4$), which is associated with polymetallic ore mineralisation (Cu, Fe and Ag) in this area [68]. In the Ornak ridge mining area, barite is found in veins with chalcopyrite, pyrite and galena (PbS). Barite frequently occurs alongside sulphide minerals in ore deposits [72]. Barite was also identified in Group II Technosols based on microscopic studies and SEM-EDS analyses of soil thin sections [18]. Contents of Pb and Zn were elevated in some profiles representing Group II Technosols (e.g., Profiles 9 and 10) (Figure 2). Lead and Zn are related to the remnants of polymetallic ores occurring in mining waste deposited in dumps [68].

Group III Technosols (Profiles 11–13) were characterised by elevated contents of Cu, Pb, As and Sb, likely originating from historical metallurgical activities. These PTTE commonly occur in metallurgical slags where they are trapped during cooling, forming metallic aggregates (e.g., native Cu, Pb and Fe) or mineral phases (e.g., sulphides and oxides) [73]. Metal(loid)s are subsequently released into surrounding soils during slag weathering, creating persistent geochemical anomalies [74–76]. The presence of Cu, As and Sb reflected their association with polymetallic ores processed in smelters. High contents of PTTE are typical of metallurgical waste [77]. The elevated contents of metal(loid)s in metallurgical waste reflect the original ore composition, processing chemistry and metallurgical partitioning behaviours, leading to enrichment of slags in various metal(loid)s, as metallurgical processes are not fully effective in the extraction of metal(loid)s from ore [13,78]. Extremely high contents of Cu (>10,000 mg·kg^{-1}), As (up to 901 mg·kg^{-1}) and Hg (>50 mg·kg^{-1}) in the 3C horizon of P12 were most likely due to the fact that it was a layer of crushed rocks rich in polymetallic ore. That horizon contained mining waste (not metallurgical waste), which were preserved in the examined soil profile as a separate layer buried subsequently by newer anthropogenic materials.

4.3. Assessment of Mobility of PTTE in the Studied Technosols Based on BCR Sequential Extraction

BCR sequential extraction revealed distinct chemical behaviours of PTTE across the three Technosol groups, strongly influenced by their properties, which were controlled by the mineral and chemical composition of the parent materials. These findings aligned with the results of other authors [20,61], who emphasised that metal(loid)s fractionation in soils is governed by geogenic and anthropogenic factors.

In Group I Technosols, the predominance of residual fractions (F4) for PTTE such as Cu, Zn, Pb, As, Co, Ni and Cr reflected low mobility of these elements. Therefore, carbonate minerals present in these soils likely play the most important role in immobilisation of these elements by maintaining the soil pH at a high level (Table S2). The strong positive correlation between $CaCO_3$ and pH ($r = 0.81$; $p < 0.05$; Table S3) confirmed the dominant effect of calcium carbonates on soil pH. High pH of soil limits the solubility of many PTTE, causing them to form weakly soluble mineral phases [20]. This favours the precipitation of metals as insoluble carbonates or hydroxides, effectively reducing their solubility and bioavailability [30,59,79]. Additionally, carbonate minerals like calcite and dolomite have relatively high chemical stability, particularly in soils having high pH [80]. Under such conditions, carbonates provide surfaces for adsorption, which further immobilises metals by binding metal ions and preventing their release into the soil solution [81]. Together, these processes decrease the bioavailability and leaching potential of metals, contributing to their retention primarily within the residual soil fraction [30]. In Profile 3, representing Group I Technosols, oxidisable Cu (F3, 80%) and reducible Zn and Pb (F2, up to 91%) (Figure 3) forms occurred in the topsoil, which suggested that SOM and Fe/Mn oxides, respectively, contributed to the binding of Cu, Zn and Pb [82]. Cadmium seemed to be a rather mobile element in all Group I Technosols, as it occurred mostly in F2 (metals supposed to be

related to Fe/Mn oxides). Cadmium tends to be more mobile in soils than many other PTTE because it often occurs in easily soluble or exchangeable forms in soils [67,83]. The high residual Cd (F4, 78%) in Profile 1 subsoil (Figure 3) contrasted with its typical high or moderate mobility, likely due to carbonate co-precipitation.

In Group II Technosols (acidic soils developed from aluminosilicate mining waste), the predominance of the reducible fraction (F2) of Co, Pb, Cu, Ag, Mn and Ba reflected the important role of Fe and Mn oxides in controlling the mobility of these elements. The low pH range (3.6–6.0) in soils enhances the solubility of such metals as Pb, Zn, Cu, Cd and others, promoting desorption and leaching [84–86]. BCR analyses showed that the most mobile elements in Group II Technosols were Mn, Cu and Zn (Figures 3 and 5), as a considerable share of these metals occurred in F1 in these soils. Furthermore, a rather small amount of investigated elements in F3 in Group II Technosols (except for Cu, Ni and Cr in some studied soils) indicated that SOM has a limited metal stabilising effect, which corresponded with the observations in other Technosols [66]. Moreover, Cd was a mobile element in Profile 5. On the other hand, some elements typically mobile in acidic soils (e.g., Zn, Cd and Ni) often occurred in the residual fraction (F4) in Group II Technosols. Such a feature is most likely due to the physical blocking of metal-bearing minerals inside quartz or aluminosilicate grains, which were the major minerals occurring in the studied Technosols [17]. This makes it impossible for the reagents used during the first three steps of sequential extraction to dissolve these minerals. Quartz and aluminosilicates are minerals resistant to weathering [87]; therefore, they are not dissolved during the first three steps of sequential extraction and constituted part of F4. Moreover, these metals can be present as stable sulphides and oxides, such as chalcopyrite and hematite, which further limit their mobility until they dissolve or weather [88,89].

Group III Technosols from historical smelting areas displayed the most complex chemical behaviours of PTTE. BCR analysis showed that Co, Mn, Ni, Ba, Sr, Pb, Zn and Cu were the most mobile elements in soils (Figures 1–3). On the other hand, As, Sb and Cd seemed to be the least mobile in Group III Technosols. Reducible Pb (F2, up to 94%) and oxidisable Cu (F3, up to 79%) (Figure 3) indicated slag-derived metals bound to Fe/Mn oxides and SOM, respectively [11,90]. Construction materials in the 2C horizon of Profile 13 artificially elevated pH and Cr mobility [17].

Thanks to the four-step BCR analysis, it was possible to identify the contents of PTTE present in the first fraction (F1), i.e., in the most mobile forms in soil (Table 3). In Group II Technosols (Profiles 9 and 10), high contents of Cu reaching up to 174 $mg \cdot kg^{-1}$ (horizon C1 of P10) were found in F1. Relatively high contents of Cu and Sb (43 and 7 $mg \cdot kg^{-1}$, respectively) were recorded in the 3C horizon of Profile 12, which was a layer of ore-bearing rocks (not metallurgical waste) preserved within the soil profile. The highest content of Zn in F1 was measured at the old steelworks in Kuźnice (P13), amounting to 50 $mg \cdot kg^{-1}$ (horizon AC). In other locations, the contents of Zn reached a maximum at 9 $mg \cdot kg^{-1}$ (P3, horizon O/C) or around 3–4 $mg \cdot kg^{-1}$ (P6, horizons Bw and C, respectively). In F1, Pb contents of up to 0.9 $mg \cdot kg^{-1}$ (P11, horizon A), As up to 1.2 $mg \cdot kg^{-1}$ (P3, horizon O/C), Co up to 1.1 $mg \cdot kg^{-1}$ (P9, horizon AC), Ni and Cd up to 0.3 $mg \cdot kg^{-1}$, Cr up to 0.9 $mg \cdot kg^{-1}$, Sr up to 58 $mg \cdot kg^{-1}$, Ba up to 213 $mg \cdot kg^{-1}$ and Mn up to 2242 $mg \cdot kg^{-1}$ (P13, horizon AC) were recorded. These results indicated the potential mobility of several PTTE in the studied Technosols, which could pose environmental risks through possible uptake of PTTE by plants and leaching of PTTE into groundwater and surface water, including mountain streams typically found in the vicinity of sampling points near waste disposal sites, adits, shafts and historical smelting areas. Such findings were consistent with previous studies emphasising the importance of the exchangeable fraction (F1) as a key indicator of bioavailable and mobile metals in contaminated soils [29,30,44,67,69].

Table 3. Contents of PTTE in the most mobile fraction (F1) based on BCR sequential extraction.

Soil Profile	Horizon	Depth (cm)	Cu	Zn	Pb	Cd	As	Sb	Ba	Sr	Co	Ni	Mn	Cr
			mg·kg^{-1}											
P1	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
	AC1	1–5	0.00	0.56	0.00	0.00	0.70	0.40	2.88	17.14	0.00	0.00	9.14	0.00
	AC2	5–15	0.00	0.06	0.00	0.00	0.23	0.17	1.74	13.79	0.00	0.00	0.72	0.00
	C	15–35	0.00	0.00	0.00	0.00	0.15	0.12	3.88	10.60	0.00	0.00	0.73	0.00
	2C	35–60	0.00	0.00	0.00	0.02	0.10	0.20	5.58	7.59	0.00	0.01	47.04	0.00
P2	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
	AC1	1–25	0.00	0.00	0.00	0.00	0.38	0.01	1.45	9.73	0.00	0.02	10.05	0.00
	AC2	25–45	0.00	0.00	0.00	0.00	0.54	0.12	1.11	10.22	0.00	0.00	0.47	0.00
	AC3	45–65	0.00	0.00	0.00	0.02	0.15	0.02	0.92	9.29	0.00	0.00	0.44	0.00
	2C	65–90	0.00	0.07	0.00	0.00	0.18	0.00	0.78	8.30	0.00	0.00	0.34	0.00
P3	Oe	0–6	–	–	–	–	–	–	–	–	–	–	–	–
	O/C	6–25	0.00	9.25	0.00	0.16	1.19	0.44	3.14	12.90	0.00	0.00	90.82	0.00
	AC	25–40	0.00	0.23	0.00	0.00	0.18	0.00	0.64	2.05	0.00	0.00	3.58	0.00
	BC	40–60	0.00	0.04	0.00	0.00	0.10	0.00	0.43	1.60	0.00	0.00	0.00	0.00
P4	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–13	0.00	0.41	0.01	0.00	0.00	0.00	9.11	2.37	0.00	0.00	31.81	0.00
	C1	13–35	0.00	0.03	0.00	0.00	0.00	0.00	45.03	1.36	0.00	0.00	55.72	0.00
	C2	35–60	0.00	0.00	0.00	0.00	0.00	0.00	60.29	0.74	0.00	0.00	54.51	0.00
P5	Oe	0–3	–	–	–	–	–	–	–	–	–	–	–	–
	Oa	3–10	–	–	–	–	–	–	–	–	–	–	–	–
	A	10–15	3.36	0.64	0.21	0.02	0.02	0.42	15.01	3.47	0.02	0.05	71.59	0.00
	Bw	15–20	6.41	0.32	0.05	0.04	0.11	0.31	26.35	4.53	0.05	0.01	115.61	0.00
	C	20–45	2.74	0.14	0.00	0.20	0.04	0.48	35.18	6.88	0.00	0.00	24.30	0.00
P6	Oe	0–2	–	–	–	–	–	–	–	–	–	–	–	–
	Oa	2–10	–	–	–	–	–	–	–	–	–	–	–	–
	ABw	10–20	9.80	3.12	0.00	0.00	0.00	0.22	65.92	1.91	0.44	0.13	296.36	0.00
	C	20–65	99.48	3.98	0.02	0.00	1.06	1.36	147.88	12.41	0.00	0.19	120.97	0.00
P7	Oe	0–2	–	–	–	–	–	–	–	–	–	–	–	–
	AC	2–15	0.73	1.23	0.49	0.00	0.10	0.00	3.73	0.21	0.00	0.00	17.86	0.00
	C	15–50	0.00	0.52	0.00	0.00	0.00	0.00	8.11	0.11	0.00	0.00	32.26	0.00

Table 3. *Cont.*

Soil Profile	Horizon	Depth (cm)	Cu	Zn	Pb	Cd	As	Sb	Ba	Sr	Co	Ni	Mn	Cr
			mg·kg^{-1}											
P8	Oe	0–4	–	–	–	–	–	–	–	–	–	–	–	–
	AC	4–15	2.29	0.63	0.05	0.00	0.02	2.18	49.60	1.14	0.01	0.00	261.77	0.00
	C1	15–35	4.04	0.27	0.05	0.00	0.00	0.99	55.54	0.79	0.00	0.00	321.57	0.00
	C2	35–55	3.66	0.38	0.00	0.00	0.00	0.64	46.23	0.61	0.00	0.00	343.39	0.00
P9	Oi	0–2	–	–	–	–	–	–	–	–	–	–	–	–
	AC	2–10	56.93	1.26	0.16	0.00	0.18	2.40	141.50	0.98	1.14	0.02	230.44	0.00
	C1	10–40	131.25	0.92	0.01	0.00	0.59	4.20	162.29	1.34	0.16	0.00	168.25	0.00
	C2	40–80	105.88	0.71	0.03	0.00	0.60	3.89	173.58	1.64	0.10	0.00	163.39	0.00
P10	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
	AC	1–10	101.55	1.26	0.63	0.00	0.03	2.43	85.42	0.33	0.24	0.00	156.77	0.00
	C1	10–50	174.07	1.36	0.05	0.00	0.09	3.30	101.12	0.37	0.00	0.00	92.91	0.00
	C2	50–70	154.26	1.04	0.03	0.00	0.02	2.88	87.79	0.47	0.00	0.00	66.63	0.00
P11	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–15	1.17	0.00	0.86	0.01	0.10	0.16	7.43	5.58	0.00	0.00	29.27	0.00
	C1	15–30	0.00	0.00	0.00	0.00	0.27	0.15	6.05	7.54	0.00	0.00	17.98	0.00
	C2	30–45	0.00	1.39	0.00	0.17	0.00	0.39	5.98	6.51	0.00	0.00	15.08	0.00
	C3	45–60	0.00	0.00	0.00	0.00	0.14	0.03	6.21	8.26	0.00	0.00	5.97	0.00
P12	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
	A	1–20	1.21	0.05	0.00	0.01	0.04	0.23	16.34	5.09	0.00	0.02	22.39	0.00
	C1	20–28	5.10	0.08	0.04	0.02	0.10	2.18	58.11	4.26	0.00	0.00	7.77	0.00
	2C	28–50	0.00	0.28	0.00	0.00	0.06	1.38	18.39	16.43	0.00	0.03	10.09	0.00
	3C	50–60	42.48	1.19	0.00	0.02	0.00	6.45	35.90	5.18	0.00	0.02	4.95	0.00
	4C	60–75	2.14	0.62	0.00	0.00	0.03	4.20	29.22	6.78	0.00	0.00	4.06	0.00
P13	Oi	0–1	–	–	–	–	–	–	–	–	–	–	–	–
	AC	1–15	0.00	49.69	0.00	0.32	0.63	0.31	212.47	58.37	0.00	0.25	2241.64	0.87
	2C	15–25	0.00	0.52	0.00	0.00	0.21	0.04	20.03	16.86	0.00	0.02	104.27	0.00

Explanation: – not analysed.

4.4. Relationship Between Element Fractionation and Soil Properties

Table S3 presents the correlation coefficients between soil pH, carbonate content, TOC and the concentrations of elements in different BCR fractions (F1–F4). Correlation of pH with contents of elements in fractions (F1–F4) showed negative correlations between soil pH and contents of Cu, Zn, Pb, Sb, Ba, Co and Mn in F1 (Table S3), which was considered to be the most mobile fraction. This indicated that the lower the soil pH, the higher the contents of the aforementioned elements in F1. Therefore, in acidic soils, one should expect the highest mobility of Cu, Zn, Pb, Sb, Ba, Co and Mn. On the other hand, correlations between soil pH and contents of As and Sr in F1 (Table S3) were positive, which indicated that the higher the pH (within the ranges of pH found in the studied soils), the higher the mobility of As and Sr in the studied soils.

Statistical analyses showed significant negative correlations between carbonate contents and Cu, Zn, Pb, Sb, Ba, Co and Mn concentrations in F1 (Table S3). These results showed that the occurrence of carbonates in soils reduced the mobility of the aforementioned elements. This result perfectly fit the aforementioned correlation between element concentrations and pH.

Statistical analyses also showed significant positive correlations between TOC contents and Zn, Pb and Cr concentrations in F3 (Table S3), which was considered to be a fraction related to SOM. These results showed that the aforementioned elements had a high affinity for SOM. On the other hand, As was an element not related to SOM in the studied Technosols, which was corroborated by the negative correlation between TOC contents and concentration of As in F3. These findings were in line with the results of other authors [91–93].

4.5. Geochemical Features of Technosol Groups Based on the Total Contents of PTTE and REE

The total PTTE and REE contents revealed distinct geochemical signatures across the three groups of Technosols, highlighting the critical role of the parent material in controlling the chemical composition of the investigated soils, which was postulated in our previous study [17].

Group I Technosols (in particular Profiles 1 and 2), developed from carbonate-rich mining waste, were characterised by t elevated concentrations of siderophile elements (Co and Ni) (Figure 1; Table S1), as well as Fe and Mn [17], which reflected the geogenic origin of these elements from rocks containing dispersed Fe- and Mn-ore bearing minerals. Group I Technosols were also characterised by relatively high total REE contents (up to 786 mg·kg^{-1}) (in comparison with other soils), which was most likely due to the high abundance of REE-bearing minerals and the strong affinity of REE for carbonate minerals in rocks [94].

Group II Technosols (Profiles 5–10), developed from aluminosilicate mining waste containing remnants of polymetallic ores, exhibited very high variability in PTTE contents, with notable enrichments in chalcophile elements (Cu, Mo, Hg, As, Sb and Bi), but also Ba, Sr, U and Th (Figure 1; Table S1). These patterns reflected the polymetallic nature of ores scattered in the parent rocks. The lower total REE contents (up to 346 mg·kg^{-1}) (Table 2) compared to Group I suggested most likely a lower abundance of REE-bearing minerals in the parent material.

Group III Technosols (Profiles 11–13), containing waste from smelting activities, displayed the most complex contamination patterns. Excluding the 3C horizon from Profile 12 (as it was most likely a layer of ore-bearing rocks preserved in the soil profile), it should be stated that these soils were enriched in a number of metal(loids) (Cu, As, Sb, Ba, Hg, Co and Ag) coming from the ores processed in smelters, which were mostly represented

by polymetallic ores. The relatively low REE contents (<237 $mg \cdot kg^{-1}$) (Table 2) was also a feature of Group III Technosols.

5. Conclusions

1. The studied Technosols in the Tatra Mountains exhibit significant contamination with several PTTE exceeding Polish regulatory limits for Cu, Zn, Pb, Mo, Hg, As, Co, Ni and Ba.
2. The three Technosol groups distinguished in the study are characterised by different geochemical features. Group I Technosols (near-neutral soils developed from Fe/Mn-ore and carbonate-bearing mining waste) are particularly enriched in Co, Ni and REE and contain Cu, Zn, Pb, As, Co, Ni and Cr mostly in immobile forms.
3. Group II Technosols (acidic soils developed from polymetallic ore-bearing aluminosilicate mining waste) contained elevated concentrations of Cu, Zn, Hg, As, Sb, Bi, Co, Ag, Ba, Sr, U and Th; the contents of REE were lower than in Group I Technosols. PTTE (in particular Mn, Cu and Zn) exhibited the highest mobility among the studied soils, and Fe and Mn oxides seem to control the mobility of Co, Pb, Cu, Ag, Mn and Ba.
4. Group III Technosols (soils developed in smelting-affected areas and containing metallurgical waste) contained high total concentrations of Cu, As, Sb, Ba, Hg, Co and Ag, the lowest REE contents among the studied soils and were characterised by complex behaviours of PTTE, with Pb and Cu having high affinity to Fe/Mn oxides and organic matter, respectively.
5. The study showed relationships between element fractionation and soil properties such as pH, presence of carbonates and contents of SOM. Statistical analyses showed increases in Cu, Zn, Pb, Sb, Ba, Co and Mn mobility along with decreases in soil pH and carbonate contents. However, the behaviours of As and Sr exhibited the opposite trend: the higher the pH, the higher the mobility of these elements. The results also showed that Zn, Pb and Cr have a high affinity for SOM. On the other hand, As is an element whose mobility is not related to SOM in the studied Technosols.
6. The four-step BCR analysis allowed for the identification of PTTE in the most mobile forms (fraction F1). High contents of Cu, Zn, Sb, Pb, As, Co, Ni, Cd, Cr, Sr, Ba and Mn were found in F1 in specific horizons of several Technosols, indicating that these elements may be readily mobilised. This highlights the potential environmental risks of PTTE related to possible uptake of PTTE by plants and leaching of PTTE into groundwater and surface water.
7. The findings highlight opportunities for further research to better understand the mechanisms driving PTTE mobility in contaminated soils. Future studies could explore the accumulation of PTTE in plants, as well as how pH variations and interactions with groundwater and surface water influence the mobilisation of individual elements. Such research may also support predictions of how PTTE could spread from contaminated soils, which could improve environmental risk assessment in Tatra National Park.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min15090988/s1, Table S1: Total concentrations of trace elements in the studied soils; Table S2: Selected chemical properties of the studied soils [17]; Table S3: Statistical analysis.

Author Contributions: Conceptualization, M.T., Ł.U., W.K. and A.P.; methodology, M.T., Ł.U., W.K., A.P. and F.J.M.-P.; validation, M.T., Ł.U., W.K., A.P. and F.J.M.-P.; investigation, M.T., Ł.U., W.K., A.P. and F.J.M.-P.; data curation, M.T. and Ł.U.; writing—original draft preparation, M.T., Ł.U. and A.P.; writing—review and editing, M.T., Ł.U., W.K., A.P. and F.J.M.-P.; visualization, M.T.; supervision, Ł.U.

and W.K.; project administration, M.T.; funding acquisition, M.T. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Science Centre, Poland, under research project no. 2021/41/N/ST10/03129.

Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Materials, and further inquiries can be directed to the corresponding author.

Acknowledgments: The Minister of Climate and Environment of Poland, as well as the Director of Tatra National Park (TNP), are acknowledged for giving permission to conduct studies in the TNP. Maria Król and Magdalena Sitarz (TNP), as well as Arletta Kochańska-Jeziorska, are acknowledged for their help with field work and in finding the literature related to the topic of the study. María del Carmen Carrasco Sierra (Universidad de Granada, Spain) is acknowledged for her assistance with laboratory analyses.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

BCR	The modified European Community Bureau of Reference
F	Fraction
ICP-MS	Inductively coupled plasma-mass spectroscopy
ICP-OES	Inductively coupled plasma-optical emission spectrometry
P	Profile
PTTE	Potentially toxic trace elements
REE	Rare earth elements
SEM-EDS	Scanning electron microscope—energy dispersive X-ray spectroscopy
SOM	Soil organic matter
TNP	Tatra National Park
TOC	Total organic carbon

References

1. Skrzydłowski, T. *Przewodnik Przyrodniczy po Tatrach Polskich*; Wydawnictwo Tatrzańskiego Parku Narodowego: Zakopane, Poland, 2019; pp. 1–432.
2. Jost, H. *O górnictwie i Hutnictwie w Tatrach Polskich*; Wydawnictwo Naukowo-Techniczne: Warsaw, Poland, 1962; pp. 1–182. (In Polish)
3. Górecki, J.; Sermet, E. *Hawiarskie Szlaki Tatr Polskich, Dzieje Górnictwa–Element Europejskiego Dziedzictwa Kultury*; Oficyna Wydawnicza Politechniki Wrocławskiej: Wrocław, Poland, 2012. (In Polish)
4. Zwoliński, S. Badania nad Historią Górnictwa i Hutnictwa w Tatrach Polskich. *Etnogr. Pol.* **1962**, *6*, 163–191. (In Polish)
5. Jach, R. Ślady dawnego wydobycia rud manganu w Tatrach Zachodnich. *Przegląd Geol.* **2002**, *50*, 1159–1164. (In Polish)
6. Gawęda, A. How to find a gold on the touristic path-a gold-mining in the Tatra Mts. *Geoturystyka* **2010**, *2*, 59–64. [CrossRef]
7. Kabała, C.; Greinert, A.; Charzyński, P.; Uzarowicz, Ł. Technogenic soils—Soils of the year 2020 in Poland. Concept, properties and classification of technogenic soils in Poland. *Soil Sci. Annu.* **2020**, *71*, 267–280. [CrossRef]
8. IUSS Working Group WRB. World Reference Base for Soil Resources. In *International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*, 4th ed.; International Union of Soil Sciences (IUSS): Vienna, Austria, 2022.
9. Néel, C.; Bril, H.; Courtin-Nomade, A.; Dutreuil, J.P. Factors affecting natural development of soil on 35-year-old sulphide-rich mine tailings. *Geoderma* **2003**, *111*, 1–20. [CrossRef]
10. Grünewald, G.; Kaiser, K.; Jahn, R. Alteration of secondary minerals along a time series in young alkaline soils derived from carbonatic wastes of soda production. *Catena* **2007**, *71*, 487–496. [CrossRef]
11. Huot, H.; Simonnot, M.O.; Watteau, F.; Marion, P.; Yvon, J.; De Donato, P.; Morel, J.L. Early transformation and transfer processes in a Technosol developing on iron industry deposits. *Eur. J. Soil Sci.* **2014**, *65*, 470–484. [CrossRef]

12. Uzarowicz, Ł.; Charzyński, P.; Greinert, A.; Hulisz, P.; Kabała, C.; Kusza, G.; Kwasowski, W.; Pędziwiatr, A. Studies of technogenic soils in Poland: Past, present, and future perspectives. *Soil Sci. Annu.* **2020**, *71*, 281–299. [CrossRef]
13. Kierczak, J.; Pietranik, A.; Piatak, N.M. Weathering of Slags. In *Metallurgical Slags: Environmental Geochemistry and Resource Potential*; Piatak, N.M., Ettler, V., Eds.; The Royal Society of Chemistry: London, UK, 2021; Volume 3, pp. 125–150.
14. Watteau, F.; Morel, J.L.; Liu, C.; Tang, Y.; Huot, H. Technosol micromorphology reveals the early pedogenesis of abandoned rare earth element mining sites undergoing reclamation in south China. *Minerals* **2025**, *15*, 514. [CrossRef]
15. Huot, H.; Simonnot, M.O.; Morel, J.L. Pedogenetic trends in soils formed in technogenic parent materials. *Soil Sci.* **2015**, *180*, 182–192. [CrossRef]
16. Uzarowicz, Ł.; Kwasowski, W.; Lasota, J.; Błońska, E.; Górka-Kostrubiec, B.; Tarnawczyk, M.; Murach, D.; Gilewska, M.; Gryczan, W.; Pawłowicz, E.; et al. Vegetation cover as an important factor affecting the properties and evolution of Spolic Technosols: A case study from a dump of the abandoned iron ore mine in central Poland. *Catena* **2025**, *254*, 108906. [CrossRef]
17. Tarnawczyk, M.; Uzarowicz, Ł.; Kwasowski, W.; Górka-Kostrubiec, B.; Pędziwiatr, A. Soil-forming factors controlling Technosol formation in historical mining and metallurgical sites in the high-alpine environment of the Tatra Mountains, southern Poland. *Catena* **2024**, *247*, 108521. [CrossRef]
18. Tarnawczyk, M.; Uzarowicz, Ł.; Pędziwiatr, A.; Kwasowski, W. Micromorphological, submicromorphological and chemical indicators of pedogenesis in Spolic Technosols developed at historical mining and metallurgical sites in the Tatra Mountains, southern Poland. *Soil Sci. Annu.* **2025**, *76*, 205499.
19. Feluch, K.; Uzarowicz, Ł. Soil development and contents of selected trace elements in Technosols on dumps of historical iron ore mines in the Jaworzynka Valley, Tatra Mountains, southern Poland. *Soil Sci. Annu.* **2025**, *76*, 205499. [CrossRef]
20. Alloway, B.; Ayres, D.C. *Chemical Principles of Environmental Pollution*, 2nd ed.; Blackie Academic: London, UK, 1997; pp. 3–85.
21. Gomez-Ros, J.M.; Garcia, G.; Peñas, J.M. Assessment of restoration success of former metal mining areas after 30 years in a highly polluted Mediterranean mining area: Cartagena-La Unión. *Ecol. Eng.* **2013**, *57*, 393–402. [CrossRef]
22. Pellegrini, S.; García, G.; Peñas-Castejon, J.M.; Vignozzi, N.; Costantini, E.A.C. Pedogenesis in mine tails affects macroporosity, hydrological properties, and pollutant flow. *Catena* **2016**, *136*, 3–16. [CrossRef]
23. Dradrach, A.; Karczewska, A.; Szopka, K. Arsenic accumulation by red fescue (*Festuca rubra*) growing in mine-affected soils—Findings from the field and greenhouse studies. *Chemosphere* **2020**, *248*, 126045. [CrossRef]
24. Dradrach, A.; Karczewska, A.; Szopka, K.; Lewińska, K. Accumulation of arsenic by plants growing in the sites strongly contaminated by historical mining in the Sudetes region of Poland. *Int. J. Environ. Res. Public Health* **2020**, *17*, 3342. [CrossRef]
25. Ferronato, C.; Vianello, G.; Feudis, M.D.; Vittori Antisari, L. Technosols development in an abandoned mining area and environmental risk assessment. *Appl. Sci.* **2021**, *11*, 6982. [CrossRef]
26. Castillo Corzo, M.; Peña Rodríguez, V.; Manrique Nugent, M.; Villarreyes Peña, E.; Byrne, P.; Gonzalez, J.C.; Patiño Camargo, G.; Barnes, C.H.W.; Sánchez Ortiz, J.F.; Saldaña Tovar, J.; et al. Potentially toxic elements and radionuclides contamination in soils from the vicinity of an ancient mercury mine in Huancavelica, Peru. *Soil Sci. Annu.* **2025**, *76*, 204389. [CrossRef]
27. García-Lorenzo, M.L.; Crespo-Feo, E.; Esbrí, J.M.; Higueras, P.; Grau, P.; Crespo, I.; Sánchez-Donoso, R. Assessment of potentially toxic elements in technosols by tailings derived from Pb–Zn–Ag mining activities at San Quintín (Ciudad Real, Spain): Some insights into the importance of integral studies to evaluate metal contamination pollution hazards. *Minerals* **2019**, *9*, 346. [CrossRef]
28. Kierczak, J.; Neel, C.; Aleksander-Kwaterczak, U.; Helios-Rybicka, E.; Bril, H.; Puziewicz, J. Solid speciation and mobility of potentially toxic elements from natural and contaminated soils: A combined approach. *Chemosphere* **2008**, *73*, 776–784. [CrossRef]
29. Kodirov, O.; Kersten, M.; Shukurov, N.; Peinado, F.J.M. Trace metal (loid) mobility in waste deposits and soils around Chadak mining area, Uzbekistan. *Sci. Total Environ.* **2018**, *622*, 1658–1667. [CrossRef] [PubMed]
30. Kicińska, A.; Pomykała, R.; Izquierdo-Diaz, M. Changes in soil pH and mobility of heavy metals in contaminated soils. *Eur. J. Soil Sci.* **2022**, *73*, e13203. [CrossRef]
31. Korzeniowska, J.; Krąż, P. Heavy Metals Content in the Soils of the Tatra National Park Near Lake Morskie Oko and Kasprowy Wierch—A Case Study (Tatra Mts, Central Europe). *Minerals* **2020**, *10*, 1120. [CrossRef]
32. Staszewski, T.; Łukasik, W.; Kubiesa, P. Contamination of Polish national parks with heavy metals. *Environ. Monit. Assess.* **2012**, *184*, 4597–4608. [CrossRef]
33. Kwapuliński, J.; Paprotny, L.; Paukszto, A.; Kowol, J.; Rochel, R.; Nogaj, E.; Musielińska, R.; Celinski, R. Influence of the type of tree habitat on the character of co-occurrence of Fe, Mn, Zn, Cu, Pb, Ni, Cr and Co in the soil of the Tatra Mountain National Park. *Ann. Agric. Environ. Med.* **2013**, *20*, 494–499.
34. Kwapuliński, J.; Paukszto, A.; Paprotny, Ł.; Musielińska, R.; Kowol, J.; Nogaj, E.; Rochel, R. Bioavailability of Lead, Cadmium, and Nickel in Tatra Mountain National Park Soil. *Pol. J. Environ. Stud.* **2012**, *21*, 407–413.
35. Kubica, B.; Kwiatek, W.M.; Stobiński, M.; Skiba, S.; Skiba, M.; Gołaś, J.; Kubica, M.; Tuleja-Krysa, M.; Wrona, A.; Misiak, R.; et al. Concentrations of 137Cs, 40K radionuclides and some heavy metals in soil samples of Chochołowska Valley from Tatra National Park. *Pol. J. Environ. Stud.* **2007**, *16*, 723–729.

36. Stobiński, M.; Kubica, B. Chemometric analysis of 137Cs activity and heavy metals distribution in the Tatras' soil. *Int. J. Environ. Sci. Technol.* **2017**, *14*, 1217–1224. [CrossRef]
37. Wieczorek, J.; Zadrożny, P. Content of Cd, Pb and Zn in podzols Tatra National Park. *Proc. ECOpole* **2013**, *7*, 57. (In Polish) [CrossRef]
38. Kowalska, J.B.; Gąsiorek, M.; Zadrożny, P.; Nicia, P.; Waroszewski, J. Deep subsoil storage of trace elements and pollution assessment in mountain Podzols (Tatra Mts., Poland). *Forests* **2021**, *12*, 291. [CrossRef]
39. Niemyska-Łukaszuk, J. Całkowita zawartość ołowiu w profilach rankerów Tatrzańskiego Parku Narodowego. *Zesz. Probl. Postępów Nauk. Rol.* **1999**, *467*, 429–437. (In Polish)
40. Niemyska-Łukaszuk, J.; Miechówka, A. Zawartość cynku, ołowiu i kadmu w poziomach powierzchniowych gleb obszarów nieleśnych Tatrzańskiego Parku Narodowego. *Przemiany Sr. Przyr. Tatr* **2002**, 99–103. (In Polish)
41. Miechówka, A.; Niemyska-Łukaszuk, J. Content diversity of Zn, Pb and Cd in Lithic Leptosols of the Tatra National Park (Poland). *Oecologia Mont.* **2004**, *13*, 1–5.
42. Miechówka, A.; Niemyska-Lukaszuk, J.; Gasiorek, M. Content of Zn, Pb, Cd and Ni in peat-bog and fen soils in the Tatra National Park. *Acta Agrophys.* **2002**, *67*, 163–172.
43. Miechówka, A.; Gąsiorek, M.; Zaleski, T. Contents of cadmium and nickel in soils and plants on grazed mountain glades in Tatra National Park. *Zesz. Probl. Postępów Nauk. Rol.* **1997**, *448*, 197–202.
44. Paprotny, Ł.; Kwapuliński, J.; Wianowska, D.; Gnatowski, M.; Kasprzyk-Pochopień, J.; Piekoszewski, W. A Comparison of Co-Occurrence of Special Forms of Selected Metals in Soil, on the Example of Sycamore, Beech, and Spruce Forest Complexes in Urbanized and Non-Urbanized Regions of Tatra National Park. *Pol. J. Environ. Stud.* **2024**, *33*, 4273–4282. [CrossRef] [PubMed]
45. Miechówka, A. Zawartość różnych form żelaza w rędzinach położonych powyżej górnej granicy lasu w Tatrach. *Rocz. Glebozn. Soil Sci. Annu.* **2001**, *52*, 135–143. (In Polish)
46. Miechówka, A.; Niemyska-Łukaszuk, J.; Ciarkowska, K. Heavy metals in selected non-forest soils from the Tatra National Park. *Chem. I Inżynieria Ekol.* **2002**, *9*, 1433–1438.
47. Paukszto, A.; Mirosławski, J. Using stinging nettle (*Urtica dioica* L.) to assess the influence of long-term emission upon pollution with metals of the Tatra National Park area (Poland). *Atmos. Pollut. Res.* **2019**, *10*, 73–79. [CrossRef]
48. Ciarkowska, K.; Miechówka, A. Identification of the factors determining the concentration and spatial distribution of Zn, Pb and Cd in the soils of the non-forest Tatra Mountains (southern Poland). *Environ. Geochem. Health* **2022**, *44*, 4323–4341. [CrossRef]
49. Demková, L.; Bobuľská, L.; Árvay, J.; Homolová, Z.; Michalko, M.; Bálintová, M. Potentially toxic elements in soil and air along an altitudinal gradient in Tatra National Park. *J. Geochem. Explor.* **2023**, *252*, 107268. [CrossRef]
50. Van Reeuwijk, L.P. *Procedures for Soil Analysis*; Technical Paper 9; ISRIC: Wageningen, The Netherlands, 2002.
51. Pansu, M.; Gautheyrou, J. *Handbook of Soil Analysis. Mineralogical, Organic and Inorganic Methods*; Springer: Berlin/Heidelberg, Germany, 2006.
52. Soil Science Division Staff. *Soil Survey Manual*; Ditzler, C., Scheffe, K., Monger, H.C., Eds.; USDA Handbook 18; Government Printing Office: Washington, DC, USA, 2017.
53. Ure, A.M.; Quevauviller, P.; Muntau, H.; Griepink, B. Speciation of heavy metals in soils and sediments—An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. *Int. J. Environ. Anal. Chem.* **1993**, *51*, 135–151. [CrossRef]
54. Mossop, K.F.; Davidson, C.M. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. *Anal. Chim. Acta* **2003**, *478*, 111–118. [CrossRef]
55. Rauret, G.; López-Sánchez, J.F.; Sahuquillo, A.; Rubio, R.; Davidson, C.; Ure, A.; Quevauviller, P. Improvement of the BCR three-step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* **1999**, *1*, 57–61. [CrossRef]
56. Chancellery of the Sejm of the Republic of Poland. Regulation of the Minister of Climate and Environment of 31 October 2024 Amending the Regulation on the Method of Conducting the Assessment of Ground Surface Pollution, 2024, No. 2024, Item 1657. Available online: https://isap.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20240001657 (accessed on 13 September 2025).
57. Charzyński, P.; Plak, A.; Hanaka, A. Influence of the soil sealing on the geoaccumulation index of heavy metals and various pollution factors. *Environ. Sci. Pollut. Res.* **2017**, *24*, 4801–4811. [CrossRef]
58. Kabata-Pendias, A.; Mukherjee, A.B. *Trace Elements from Soil to Human*; Springer: Berlin/Heidelberg, Germany, 2007; pp. 283–319.
59. Kabata-Pendias, A.; Szteke, B. *Trace Elements in Abiotic and Biotic Environments*; Taylor & Francis Group: Boca Raton, FL, USA, 2015; p. 468.
60. Sujith, P.P.; Gonsalves, M.J.B.D. Ferromanganese oxide deposits: Geochemical and microbiological perspectives of interactions of cobalt and nickel. *Ore Geol. Rev.* **2021**, *139*, 104458. [CrossRef]
61. Kabata-Pendias, A. *Trace Elements in Soils and Plants*, 3rd ed.; CRC Press: Boca Raton, FL, USA, 2000; p. 432. [CrossRef]
62. Pingitore, N.E.; Eastman, M.P. Barium partitioning in carbonates: Theory and applications. *AAPG Bull.* **1984**, *68*, 516. [CrossRef]

63. Wu, K.; Ueno, Y.; Surma, J.; Nakajo, C. Separate determination of strontium and barium mass fractions in calcite and dolomite in carbonate rocks by a multi-step sequential leaching procedure. *Geostand. Geoanalytical Res.* **2025**, 1–19. [CrossRef]
64. Canet, C.; Anadón, P.; Alfonso, P.; Prol-Ledesma, R.M.; Villanueva-Estrada, R.E.; García-Vallès, M. Gas-seep related carbonate and barite authigenic mineralization in the northern Gulf of California. *Mar. Pet. Geol.* **2013**, *43*, 147–165. [CrossRef]
65. Karczewska, A.; Lewińska, K.; Agata, M.; Krysiak, A. Soil pollution by arsenic within the allotment gardens in Zloty Stok. *Ecol. Chem. Eng.* **2010**, *17*, 927–933.
66. Tarnawczyk, M.; Uzarowicz, Ł.; Perkowska-Pióro, K.; Pędziwiatr, A.; Kwasowski, W. Effect of land reclamation on soil properties, mineralogy and trace-element distribution and availability: The example of technosols developed on the tailing disposal site of an abandoned Zn and Pb mine. *Minerals* **2021**, *11*, 559. [CrossRef]
67. Uzarowicz, Ł.; Swęd, M.; Kwasowski, W.; Pędziwiatr, A.; Kaczmarek, D.; Koprowska, D.; Górka-Kostrubiec, B.; Pawłowicz, E.; Murach, D. Initial pedogenic processes, mineral and chemical transformations and mobility of trace elements in Technosols on dumps of the former copper mines in Miedziana Góra and Miedzianka, the Świętokrzyskie Mts., south-central Poland. *Catena* **2024**, *245*, 108293. [CrossRef]
68. Sitarz, M.; Gołębiowska, B.; Nejbert, K.; Dimitrova, D.; Milovský, R. Hydrothermal ore mineralization from the Polish part of the Tatra Mts., Central Western Carpathians. *Geol. Geophys. Environ.* **2021**, *47*, 159–179. [CrossRef]
69. Swęd, M.; Uzarowicz, Ł.; Duczmal-Czernikiewicz, A.; Kwasowski, W.; Pędziwiatr, A.; Siepak, M.; Niedzielski, P. Forms of metal(loid)s in soils derived from historical calamine mining waste and tailings of the Olkusz Zn–Pb ore district, southern Poland: A combined pedological, geochemical and mineralogical approach. *Appl. Geochem.* **2022**, *139*, 105218. [CrossRef]
70. Hazen, R.M.; Golden, J.; Downs, R.T.; Hystad, G.; Grew, E.S.; Azzolini, D.; Sverjensky, D.A. Mercury (Hg) mineral evolution: A mineralogical record of supercontinent assembly, changing ocean geochemistry, and the emerging terrestrial biosphere. *Am. Mineral.* **2012**, *97*, 1013–1042. [CrossRef]
71. Jolly, J.L.; Van Heyl, A. *Mercury and Other Trace Elements in Sphalerite and Wallrocks from Central Kentucky, Tennessee, and Appalachian Zinc Districts*; United States Government Printing Office: Washington, DC, USA, 1968; p. 29. [CrossRef]
72. Tombros, S.F.; Seymour, K.S.; Williams-Jones, A.E.; Zhai, D.; Liu, J. Origin of a barite-sulfide ore deposit in the Mykonos intrusion, Cyclades: Trace element, isotopic, fluid inclusion and Raman spectroscopy evidence. *Ore Geol. Rev.* **2015**, *67*, 139–157. [CrossRef]
73. Warchulski, R. Zn-Pb slag crystallization: Evaluating temperature conditions on the basis of geothermometry. *Eur. J. Mineral.* **2016**, *28*, 375–384. [CrossRef]
74. Kierczak, J.; Potysz, A.; Pietranik, A.; Tyszka, R.; Modelska, M.; Néel, C.; Ettler, V.; Mihaljevič, M. Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland). *J. Geochem. Explor.* **2013**, *124*, 183–194. [CrossRef]
75. Potysz, A.; van Hullebusch, E.D.; Kierczak, J.; Grybos, M.; Lens, P.N.; Guibaud, G. Copper metallurgical slags–current knowledge and fate: A review. *Crit. Rev. Environ. Sci. Technol.* **2015**, *45*, 2424–2488. [CrossRef]
76. Tyszka, R.; Pietranik, A.; Potysz, A.; Kierczak, J.; Schulz, B. Experimental simulations of ZnPb slag weathering and its impact on the environment: Effects of acid rain, soil solution, and microbial activity. *J. Geochem. Explor.* **2021**, *228*, 106808. [CrossRef]
77. Ilutiu-Varvara, D.A. Researching the hazardous potential of metallurgical solid wastes. *Pol. J. Environ. Stud.* **2016**, *25*, 147–152. [CrossRef]
78. Kupczak, K.; Warchulski, R.; Ettler, V.; Mihaljevič, M. The impact of buried historical copper slags on contemporary soil contamination. *J. Geochem. Explor.* **2025**, *273*, 107743. [CrossRef]
79. Ding, Q.; Cheng, G.; Wang, Y.; Zhuang, D. Effects of natural factors on the spatial distribution of heavy metals in soils surrounding mining regions. *Sci. Total Environ.* **2017**, *578*, 577–585. [CrossRef] [PubMed]
80. Doner, H.E.; Lynn, W.C. Carbonate, Halide, Sulfate, and Sulfide Minerals. In *Minerals in Soil Environments*; Dixon, J.B., Weed, S.B., Eds.; American Society for Agronomy and the Soil Science Society of America: Madison, WI, USA, 1989; pp. 279–330.
81. Lee, H.H. Adsorption characteristics of cadmium onto calcite and its agricultural environmental relevance. *Heliyon* **2024**, *11*, e40241. [CrossRef]
82. Kubová, J.; Matúš, P.; Bujdoš, M.; Hagarová, I. Utilization of optimized BCR three-step sequential and dilute HCl single extraction procedures for soil–plant metal transfer predictions in contaminated lands. *Talanta* **2008**, *75*, 1110–1122. [CrossRef]
83. Kubier, A.; Wilkin, R.T.; Pichler, T. Cadmium in soils and groundwater: A review. *Appl. Geochem.* **2019**, *108*, 104388. [CrossRef]
84. Chuan, M.C.; Shu, G.Y.; Liu, J.C. Solubility of heavy metals in a contaminated soil: Effects of redox potential and pH. *Water Air Soil Pollut.* **1996**, *90*, 543–556. [CrossRef]
85. Rieuwerts, J.S.; Thornton, I.; Farago, M.E.; Ashmore, M.R. Factors influencing metal bioavailability in soils: Preliminary investigations for the development of a critical loads approach for metals. *Chem. Speciat. Bioavailab.* **1998**, *10*, 61–75. [CrossRef]
86. Martínez, C.E.; Motto, H.L. Solubility of lead, zinc and copper added to mineral soils. *Environ. Pollut.* **2000**, *107*, 153–158. [CrossRef]
87. Wilson, M.J. Weathering of the primary rock-forming minerals: Processes, products and rates. *Clay Miner.* **2004**, *39*, 233–266. [CrossRef]

88. Sracek, O. Formation of secondary hematite and its role in attenuation of contaminants at mine tailings: Review and comparison of sites in Zambia and Namibia. *Front. Environ. Sci.* **2015**, *2*, 64. [CrossRef]
89. Tang, Y.; Sun, D.; Gou, J.; Ni, X.; Zeng, X.; Zhang, X.; Liu, W.; Liang, S.; Deng, C. Chalcopyrite geochemistry: Advancements and implications in ore deposit research. *Ore Geol. Rev.* **2025**, *179*, 106528. [CrossRef]
90. Guillevic, F.; Rossi, M.; Develle, A.-L.; Spadini, L.; Martins, J.M.F.; Arnaud, F.; Poulenard, J. Pb dispersion pathways in mountain soils contaminated by ancient mining and smelting activities. *Appl. Geochem.* **2023**, *150*, 105556. [CrossRef]
91. Romero-Freire, A.; Sierra-Aragón, M.; Ortiz-Bernad, I.; Martín-Peinado, F.J. Toxicity of arsenic in relation to soil properties: Implications to regulatory purposes. *J. Soils Sediments* **2014**, *14*, 968–979. [CrossRef]
92. Hattab, N.; Motelica-Heino, M.; Faure, O.; Bouchardon, J.L. Effect of fresh and mature organic amendments on the phytoremediation of technosols contaminated with high concentrations of trace elements. *J. Environ. Manag.* **2015**, *159*, 37–47. [CrossRef]
93. Paniagua-López, M.; Aguilar-Garrido, A.; Contero-Hurtado, J.; García-Romera, I.; Sierra-Aragón, M.; Romero-Freire, A. Ecotoxicological assessment of polluted soils one year after the application of different soil remediation techniques. *Toxics* **2023**, *11*, 298. [CrossRef]
94. Liang, T.; Li, K.; Wang, L. State of rare earth elements in different environmental components in mining areas of China. *Environ. Monit. Assess.* **2014**, *186*, 1499–1513. [CrossRef]

Warsaw, 29.09.2025

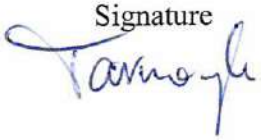
Mahgdalena Tarnawczyk
mtarnawczyk@gmail.com

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Pędziwiatr A., Martin-Peinado F.J., 2025. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. Minerals, 15(9), 988, my individual contribution to its creation consisted of the major part of the work presented in this publication, including Conceptualization, methodology, validation, investigation, data curation, writing—original draft preparation, writing—review and editing, visualization, project administration, funding acquisition.

Signature



Warsaw, 29.09.2025

Łukasz Uzarowicz
lukasz_uzarowicz@sggw.edu.pl

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Pędziwiatr A., Martin-Peinado F.J., 2025. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. Minerals, 15(9), 988, my individual contribution to its creation consisted of writing – original draft preparation, writing – review and editing, validation, supervision, methodology, investigation, data curation, conceptualization.

Signature

Warsaw 29.09.2025

Wojciech Kwasowski
Wojciech_kwasowski@sggw.edu.pl

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Pędziwiatr A., Martin-Peinado F.J., 2025. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. Minerals, 15(9), 988, my individual contribution to its creation consisted of writing – review and editing, Validation, Supervision, Methodology, Investigation, Conceptualization.

Signature

Warsaw, 29.09.2025

Artur Pędziwiatr
artur_pedziwiatr@sggw.edu.pl

Agriculture and Horticulture Discipline Council of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Pędziwiatr A., Martin-Peinado F.J., 2025. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. Minerals, 15(9), 988, my individual contribution to its creation consisted of writing – original draft preparation, writing – review and editing, validation, methodology, investigation, conceptualization.

Signature

Pędziwiatr Artur

Granada (Spain), 26th September 2025

Francisco José Martín Peinado
fjmartin@ugr.es

Agriculture and Horticulture Discipline Council
of the Warsaw University of Life Sciences

Co-authorship statement

I hereby declare that in the publication by Tarnawczyk M., Uzarowicz Ł., Kwasowski W., Pędziwiatr A., Martin-Peinado F.J., 2025. Geochemical Features and Mobility of Trace Elements in Technosols from Historical Mining and Metallurgical Sites, Tatra Mountains, Poland. Minerals, 15(9), 988, my individual contribution to its creation consisted of validation, methodology, investigation, writing, review and editing.

Signature