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The Nature of the Technosols on the Waste from Nickel Production

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Abstract: The aim of the study was to investigate the properties of the metallurgical sludge—waste from nickel production—on the landfill of a former nickel plant in Sereď, Slovakia, in relation to the technosols soil group. The sludge is a loose material which is a toxic industrial technological anthropogenic sediment of an unnatural black colour which originated from the crushing, washing, and leaching of poor iron–nickel lateritic ore in ammoniac solution and other caustics substances. The terrain reconnaissance enabled us to identify the points for the location of the probes. Here we dug seven probes and took 17 samples. In the samples the pH levels, the content of heavy metal and iron TOC, IC, C, and N, and the C:N ratio were determined. This study provides substantial empirical data on the properties of the metallurgical sludge. The results of the analyses clearly demonstrate that the sludge is a strongly alkaline material and contains toxic amounts of heavy metals (Cr, Ni). It is an artefact whose properties are unfavourable to living organisms and their communities. On the basis of the results of the probes analysis we identified the nature of the technosols on the given locality.

Keywords: metallurgical sludge; lateritic iron–nickel ore; landfill; technosols

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1. Introduction

The raw material for the production of nickel in Sereď, in the former Czechoslovakia, was the iron–nickel lateritic ore of a low-grade quality (containing 1% nickel and 0.05% cobalt per ton) imported from Albania. The ore was processed by Caron technology. The process involved the reduction roasting of the ore followed by the ammonia leaching of the reduced ore, and it is one of the ways in which nickel laterite can be treated. It was a wet metallurgical process in which 5624 t of caustic substances were used yearly [1]. The low quality of the ore caused the formation a massive landfill of waste, with an area of more than 45 ha and a volume of 9 million tons. The production of nickel was stopped in 1993 for economic and ecological reasons after 30 years. The smelting plant went through liquidation, but the massive landfill of waste remained. Immediately after the liquidation of the smelting plant the state sold the landfill to a private company in 1994. The company has been mining the metallurgical sludge for 26 years already in order to obtain the residual metals [2].

The waste has been deposited into the shape kind of a table mountain, which significantly stands out above the flat relief of the Danubian Lowland. The landfill attracts attention also due to its unnatural black color. The locality looks like an "island" in the agricultural landscape of the lowland, and so in the landscape scenery the landfill appears as an extraneous, bizarre, and barrier element. In the true sense of the word, this is an old environmental burden that has been damaging all components of the environment and the health of the region's inhabitants for more than 55 years. The landfill is composed of mainly secondary raw materials from chromium and others metals [2]. The lateritic iron–nickel ore contained 75% iron which was not used in production. Therefore, the technosols stored in the landfill contains not only nickel but also iron, copper, zinc, lead, and others. The state of the metallurgical sludge, despite the admixture of sludge from the sugar factory and fertilization with phosphorus and ground limestone, does not indicate an ongoing soil-forming process.

Based on the above, the following hypothesis was formulated: the properties of the metallurgical sludge, which have remained unchanged despite attempts to reclaim the landfill, indicate the need for a change in approach to deal with this waste in connection with the pursuit of sustainable development. We consider research in this area to be very urgent from the aspect of the health of the region's population.

2. Materials and Methods

The article provides the results of the research into the properties of the metallurgical sludge. We obtained these results on the basis of the study of archival materials, professional literature, field research, and laboratory analysis of sludge samples. Metallurgical sludge is a toxic anthropogenic sediment. The toxicity is on one hand associated with the high consumption of chemicals in the production process (during the 30 years of production 170,000 tons of caustics substances were used, Table 1), and on the other hand the sludge has a high content of iron and heavy metals and has many other adverse properties. The large quantity of the sludge (currently around 7.5 million tons) multiplies its adverse effects on the agricultural landscape.

Table 1. Metal production, chemical consumption, amount of waste, and deflation of sludge.

Metal Production	Quantity in [t]	Annual Waste Production	Waste Production over 30 Years Total [t]
Annual production of nickel and cobalt	2510	2450 [t] nickel, 60 [t] cobalt	75,300
Annual production of waste	300,000	120 [t] of waste per 1 [t] of metal	9,000,000
Annual consumption of chemicals	5624	2.25 [t] chemicals per 1 [t] of metal	168,720
Annual deflation of sludge into the air	20,000	An average of 55 [t] per day	600,000 [t]—30 years 1,140,000 [t]—57 years

Source: [1], modified by Michaeli 2019.

For the purpose of interpreting the physical–chemical properties of the metallurgical sludge in terms of possible soil forming process, we dug seven probes at the landfill, from which we took 17 samples (Figure 1). Samples of metallurgical sludge were processed in the Accredited Geoanalytical Laboratories of State Geological Institute of Dionýz Štúr in Bratislava, workplace Spišská Nová Ves, as sludge analysis requires specific protective equipment. The chromium and nickel particles are very dangerous. The chromium causes chronic bronchitis and corrodes the mucous membranes of the airways. In the upper respiratory tract, the particles corrode the mucosa and cartilage of the nasal septum.

Figure 1. Position of the probes in the landfill site, in its reclaimed and non-reclaimed parts. We can see the old nickel factory in north-east corner.

We have proposed following measurements of these physicochemical quantities in individual samples be taken: pH (H_2O); in percentage: the total organic carbon, the content of carbon and nitrogen, and the further total content of Fe_2O_3 and content of Al_2O_3. The content of nickel, chromium, cooper, and zinc elements are expressed in $mg \cdot kg^{-1}$, and the content of fractions <0.01 expressed in percentage.

The active reaction of soil pH (H_2O) was determined by the electrometric measuring method, in a suspension of one part sludge sample to 2.5 parts of boiled distilled water (20 g of dry soil sample was sifted through a sieve with 2 mm holes into a 100 mL beaker and 50 mL of boiled distilled water was added and mixed thoroughly). After 60 min under constant stirring, the suspension's pH is measured with a pH-meter. The volume of soil may be different, but the ratio between soil matter and water (1:2.5) must be maintained.

The total organic carbon (TOC) in the samples was determined by the ANALYTIC JENA MULTI HT 1300 instrument using a high-temperature oxidation method. This method involved the high-temperature oxidation of the carbon present in the samples in the oxygen stream. As a result the carbon is converted into carbon dioxide which is then detected on a non-dispersive infrared detector.

In the physical–chemical analysis of the samples, we considered the C:N ratio. The percentage of both elements was determined by elemental analysis with a thermal conductivity detector (TCD) (Analyser CHN-LECO CHN628). The cleavage of the samples took place at a high constant temperature of 1200 °C in the combustion tube under the action of a combustion catalyst. Elements C and N were absorbed from the analysed sample in the absorption column, and through increasing the temperature we induced a defined desorption of these elements and so they were detected by a thermal conductivity detector.

For analysing samples to identify and quantify the metals and heavy metals present (Ni, Cr, Cu, Zn, Al_2O_3, and Fe_2O_3) we used the analytical method of X-ray fluorescence spectrometry RFS (X-ray fluorescence spectrometer SPCTRO XEPOS). The principle of RFS consists of emitting radiation from an X-ray source. The radiation impinges on the analysed sample which then emits fluorescent radiation generated precisely due to excitation by X-rays to the detector and the amplifier (so-called secondary excitation).

The granularity of the samples took place by sieve analysis on traditional equipment, which is represented by a series of metal sieves (at least seven) placed on a vibrating stand, which is equipped with regulation of frequency and amplitude of oscillations. For sieve analysis the samples have to be dry and disassembled into aggregates.

3. Results

3.1. Study Area

The metallurgical sludge (waste from nickel and cobalt production) was stored on the landfill southwest from the town of Sered', near the former smelter plant in the northern part of the agricultural landscape of the Danubian Lowland (Figure 2), on the floodplain of the Váh river at 124 m above sea level.

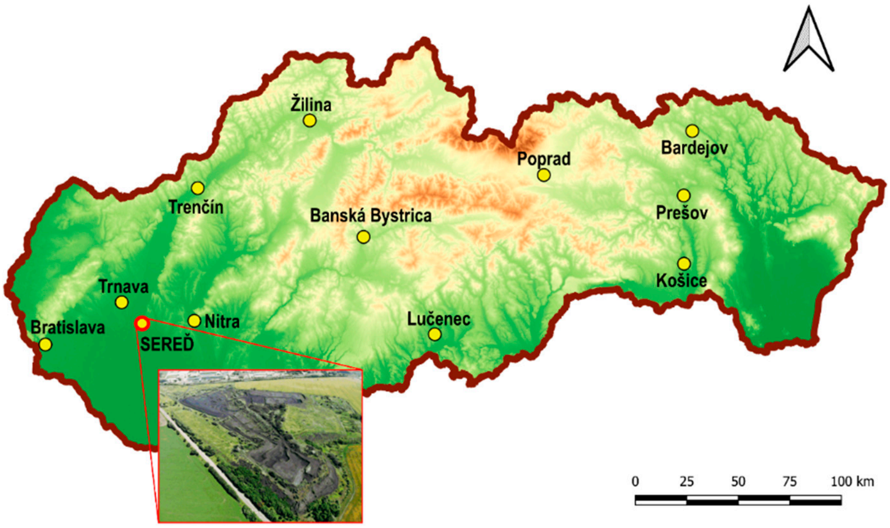

Figure 2. Localization of the survey area near Sered' town in the western part of Slovakia.

The area the body of the landfill itself is about 40 ha today. The largest width is 570 m and the length around 800–900 m. The average height is around 18 m, with highest areas of 35 m. The body of landfill is composed from two basic shapes of the relief. The first is the steep slopes (at an inclination of 45°) and the second is the slightly wavy plateau with two levels. Both forms meet in a distinct terrain edge at a relative height of 18–35 m. In the lowland landscape scenery acts to the landfill as an extraneous element. It is the remarkable shape of the relief which attracts attention also, not only due to its shape but also due to the dust particles in air which are transported during the strong winds (6°B and more), as seen in Figure 3. The landfill during the dust storm is shrouded in a large cloud of dust. The veil of dust extends 50 km into distance from the landfill.

Figure 3. Massive deflation during windy days carrying particles of chromium and other pollutants.

3.2. External Natural and Anthropogenic Factors and Conditions of Study Area

The factors and conditions of the explored territory and its surroundings are very important in terms of their mutual influences between the landfill and the lowland landscape [3]. The part of the Danubian Lowland near Sered' is composed of two groups of quaternary sediments, from a geological perspective. The first of these groups is represented by the fluvial coarse gravels and sands of the upper Pleistocene and the second is represented by clay and clay-loamy sediments of the Holocene which have a thickness of 10–12 m [4]. Another group type in this area is a young anthropogenic sediment: the metallurgical sludge. It is 57 years old and has a thickness of more than 35 m. From a chronostratigraphic point of view we can include this sediment in the Anthropocene [5]. The thickness of the formation of the quaternary sediments (the Pleistocene and Holocene) under the metallurgical sludge landfill is much smaller at 10–12 m. This is related to the creation of a bed for the sludge pond. The complex of clay and clay-loamy layers of the Holocene sediments (impermeable layers) were removed to achieve good permeability for the liquid component of the sludge.

In terms of relief the landfill is a remarkable and allochthon barrier element in the lowland landscape. It can be defined as an artificial, anthropogenic, industrial, surface, convex, and accumulation form of relief [6,7].

According the climate regionalisation of Slovakia, the landfill lies in the warm region T which has 50 or more summer days per year with a daily maximum air temperature of 25 °C or more. The landfill more precisely belongs in the T1 sub-region, which is warm and very dry with mild winters and an average January temperature of −3 °C. This region has a rainfall deficit of 100 to 150 mm per year. The average annual air temperature is 9.5 °C and the average temperature in July is 19 °C. The average number of days per year with snow cover (9–10 cm) is 40 days. The region has more than 2000 sunshine hours per year. Prevailing winds are SE and NW (51%). The region is well ventilated [8].

The water regime of the landfill is dependent on precipitation. The rainfall seeps through the sludge into the river floodplain sediments of the Váh. There are no collectors of groundwater created in the body of the landfill. We assume that directly in the landfill are soils from the group of technosols, the specifically the soil type spolic technosols/alcalic hyperartefactic [9]. The landfill has a specific vegetation cover, which is classified as metahemerobic vegetation on toxic industrial waste with minimal biogenic processes [10]. It covers only a small areas of the landfill surface (15% of vegetation was formed by reclamation).

Among other anthropogenic factors and conditions, the landfill and its surroundings are mainly influenced by the treatment of the sludge using mining machinery and by the mining itself. These processes cause secondary dustiness, which is most damaging to the environment and the health of the population.

3.3. The Properties of the Metallurgical Sludge

The metallurgical sludge is porous, strongly alkaline, loamy-sandy material of an unnaturally black colour. It is a sediment of anthropogenic origin with a high specific weight. It is very permeable and intensively absorbs infrared radiation. It has a low water retention capacity (WHC). In terms of physical composition, it is a non-homogeneous amorphous bulk material. Its composition changes locally (from place-to-place) and is especially related to the quality of ore and as well as to the individual phases of its processing.

We undertook an evaluation of the pH (H_2O) levels. The pH values in the individual probes No. 1, 2, 3, and 4 range across 7.87 to 9.30, indicating that the material is strongly alkaline. The exception is the surface horizon sample taken from probe No. 5, were the pH has reached a value of 7.6, still placing it in the category of alkaline material. The sludge is therefore alkaline and considered strongly alkaline anthropogenic material (Figure 4).

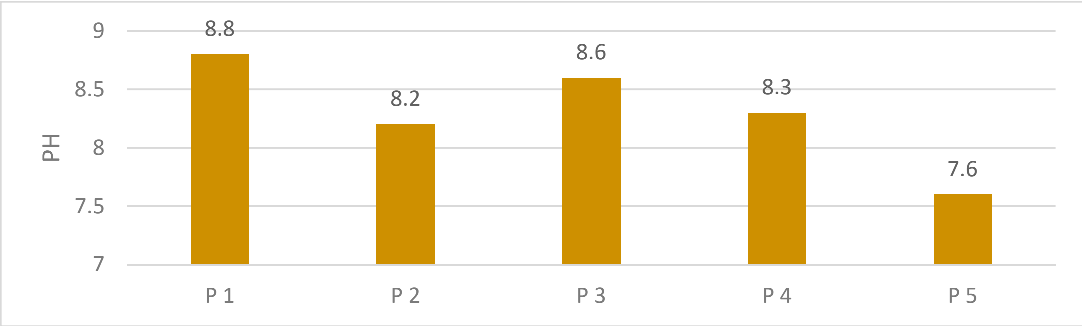

Figure 4. pH reaction in H_2O. Legend: Probes 1 to 5.

We rated the TOC, C, inorganic carbon (IC), and N and assessed the ratio of C:N. The TOC (total organic carbon) in our case is expressed as a percentage of C (carbon) per 100 g of sludge. The rating of the total organic carbon (TOC) is as follows. In probes No. 2, 3, and 5, which are located in the reclaimed part of the landfill, we found the highest amount of total organic carbon mainly in the upper horizons of the profiles of the probes (Figure 5). The content of TOC was 9.67% in probe No. 5, 9.41% in probe No. 3, and 8.15% in probe No. 2. In probes No. 1 and No. 4, the proportion of TOC had a value of 0.05–0.12%. These are extremely low contents of TOC. Probe No. 1 is located on a non-reclaimed landfill platform and probe No. 4 on a steep slope where gravitational geomorphological processes take place. The total carbon content in individual probes ranges from 0.75% to 15.8%. The percentage of inorganic carbon was obtained by subtracting the TOC value from the C value. The proportion of nitrogen ranges from 0.05% to 1.24%. The analysis of the samples shows that the smallest share of TOC, C, IC, and N are in probes No. 1 and No. 4. The quality of humus can be simply expressed by the ratio of carbon to total nitrogen. If the ratio is greater of 10:1 it indicates that the humus is low quality. From the chemical analysis of the probes the C: N ratio was found to range from 11:1 to 16:1. The value of 11:1 in probe No. 3 was the lowest. The humus is here is of very low quality.

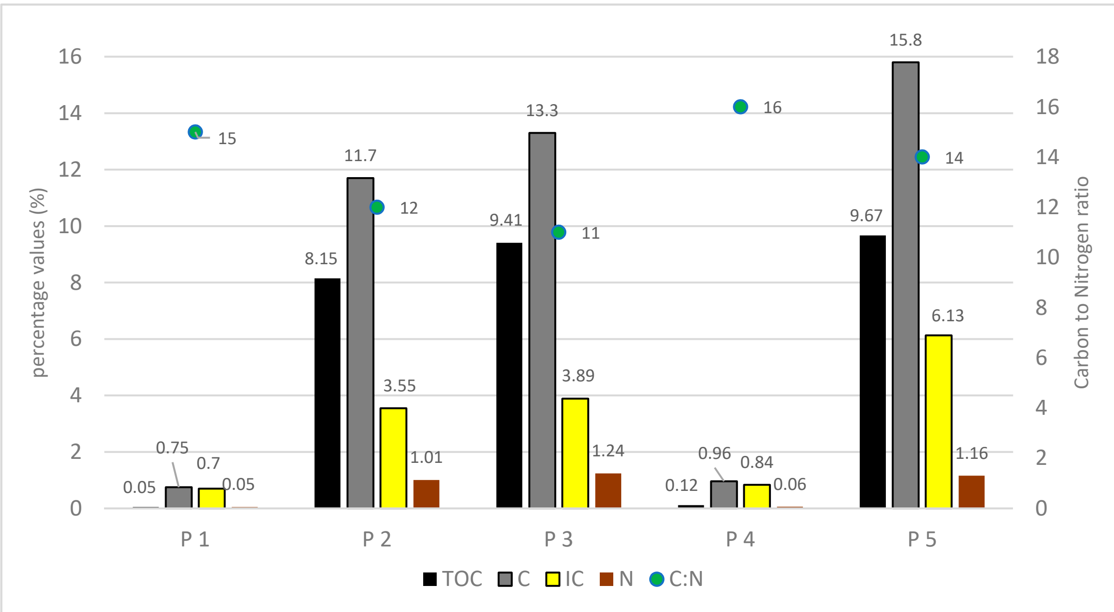

Figure 5. The content of TOC, C, IC, and N, and the C:N ratio. Legend: Probes 1 to 5, TOC: total organic carbon; C: carbon; IC: inorganic carbon; N: nitrogen; and the ratio C:N.

The lateritic iron–nickel ore which was imported from Albania to the nickel smelter in Sered' in Slovakia was mainly used for the production of nickel, partly cobalt, and contained large amounts of iron and other metals (chromium, copper, zinc, aluminum, magnesium, manganese, sodium, titanium, etc.) which left the production process as waste and was deposited into the sludge pond. As part of the analysis of the samples, we asked for the identification of some metals.

Evaluation of the content of heavy metals Ni, Cr, Cu, and Zn. The analysis of the samples shows that the high nickel content is already in the highest horizons of probes No. 1 and No. 4. (at a depth of up to 10 cm it is 2920 and 3150 mg·kg^{-1}). In probes No. 2, No. 3, and No. 5 the nickel content at a depth of up to 20 cm ranges from 641 mg·kg^{-1} to 1721 mg·kg^{-1}. At a depth of 20–50 cm in probes No. 2, No. 3, and No. 5 the nickel content increased to 3050–3120 mg·kg^{-1} (Figure 6). The chromium content in probes No. 1 and No. 4 ranges from 21,880 to 24,300 mg·kg^{-1}. In probes No. 2, No. 3, and No. 5 the chromium content ranges from 4044 to 21,370 mg·kg^{-1}. This fact is related to the reclamation of this part of the landfill but also to the technological process of ore processing (the composition of the sludge changes from place to place). The content of the copper in all probes is low from 49 to 114 mg·kg^{-1} and the content of zinc ranges from 95 to 330 mg·kg^{-1}.

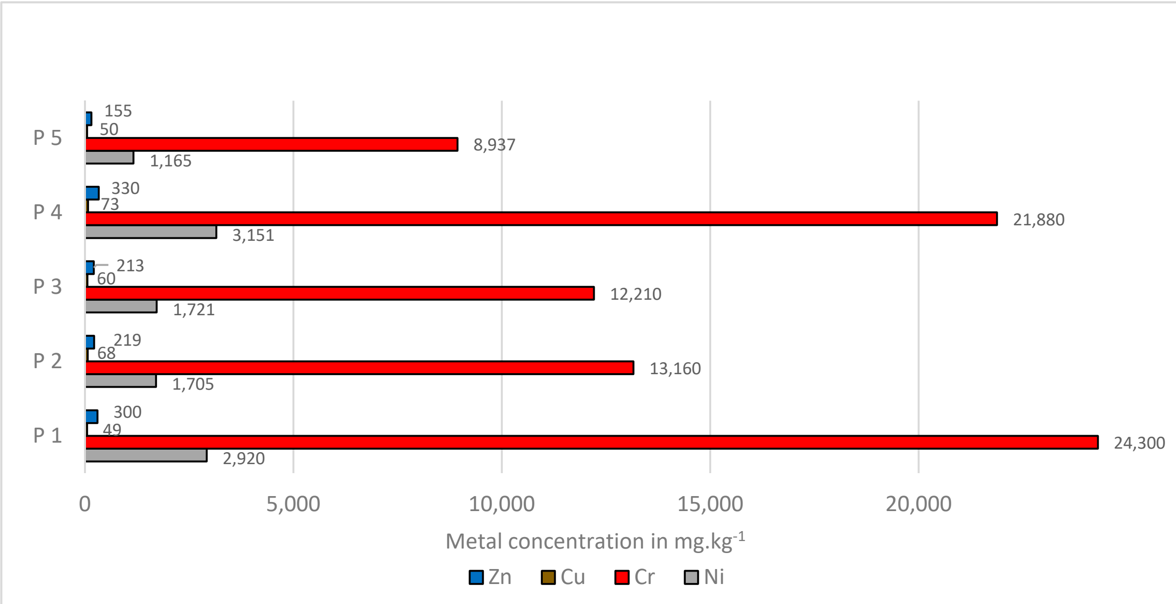

Figure 6. Content of heavy metals. Legend: Probes P1 to P5.

Evaluation of the content of Fe_2O_3 and Al_2O_3. The high proportion of Fe_2O_3 is in the upper parts of the profiles of probes No. 1 and No. 4 at a depth of 15 cm in the range of 79–75%. In probes No. 2, No. 3, and No. 5 at a depth of 15 cm the Fe_2O_3 content is 30–45% and at a depth of 50 cm it is 72–77%. The content of Al_2O_3 is, at a depth to 20 cm in probes No. 2, No. 3, and No.5, around 2% and at a the depth of 50 cm increase to 3–4%. In probes No. 1 and No. 4 the content of Al_2O_3 at a depth of 20 cm is over 3% and rises with increased depth (Figure 7).

The metals and their different content at individual depths in the profiles of the samples is probably related to the production processes that affected the sludge properties. This is because the original iron–nickel lateritic ore went through a very complex production process, and it cannot be assumed that the waste has the character of a homogenous material (Figure 8).

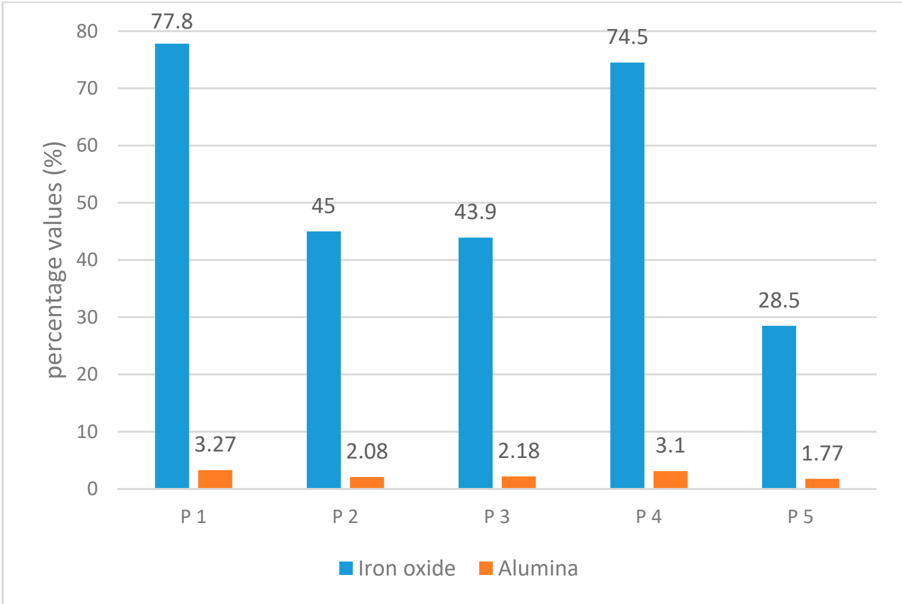

Figure 7. Content of Fe_2O_3 and Al_2O_3. Legend: Probes P1 to P5.

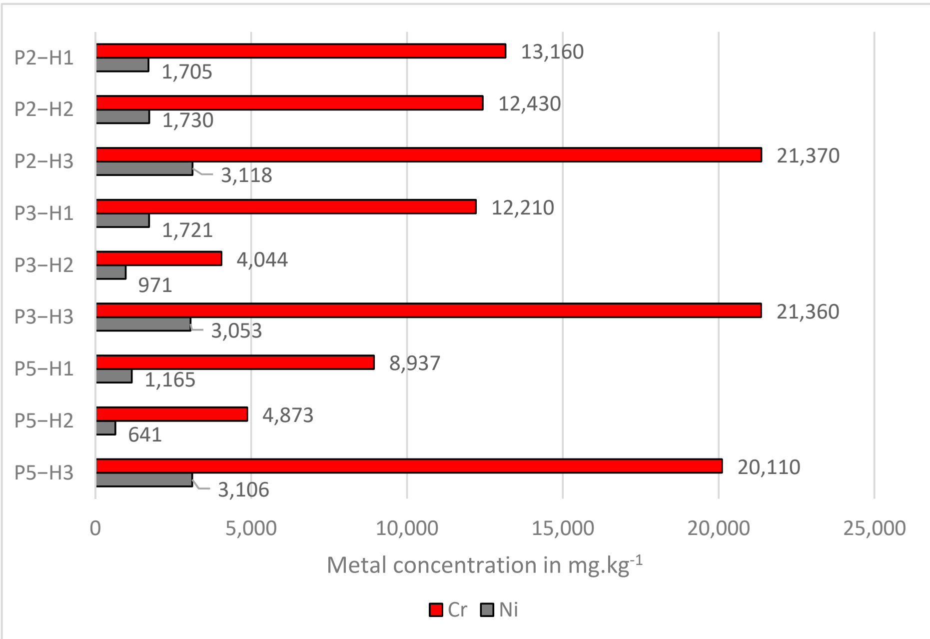

Figure 8. Comparison of the selected heavy metal contents in different depth horizons. Legend: Probes P2 to P5, H1–H3 horizons of technosols.

Granularity. According the content of the individual fractions, the metallurgical sludge is a finely granular material (Table 2). It is made up of 17% particles less than <0.01mm, 35.5% is dust (0.01–0.05 mm), and 47.4% (0.05–2.0 mm) powdered sand and sand [11].

Table 2. Analysis of the fractions of metallurgical sludge from Sered' in Slovakia.

Fractions in mm	PM_{10} < 0.01 mm	Dust 0.01–0.05 mm	Sand 0.05–2.0 mm
Share in %	17.05	35.55	47.40

Source: Materials of the FERROMIN, Company Limited [11].

The content of dust particles (>0.01 mm) was highest in probe No. 5 in the surface horizon and in the first subsurface horizon (30% and 46%, respectively). In probe No. 3, the proportion of dust particles was 35% in the first subsurface horizon and in the second subsurface horizon it was 40%. In probe No. 2 it was 28% in the first subsurface horizon. Probes No. 1 and No. 4 contained 11% dust particles in the surface horizon. The lower share of dust fractions in the surface horizons of probes No. 1 and No. 4 probably relates to deflation because the higher proportion remained in the probes where vegetation was present and the landfill relief position was less exposed position to wind activity (probes No. 5 and No. 2). At the bottom of the profiles of the probes, the proportion of dust particles was around 11% (Table 3).

Table 3. Content the dust particles of fraction >0.01 in in individual horizons of probes No. 1 to No. 5 in %.

Content of Dust Particles of Fraction >0.01 in Individual Horizon of Probes in %	Probe No. 1	Probe No. 2	Probe No. 3	Probe No. 4	Probe No. 5	Average
Surface horizon	11.1	15.5	14.2	11.9	30.2	16.0
First subsurface horizon	-	27.7	35.0	-	46.4	33.0
Second subsurface horizon	-	11.3	39.7	-	11.2	18.2
Third subsurface horizom—only in probe No.3	-	-	11.2	-	-	11.2

Source: ŠGUDŠ Bratislava, Accredited Geoanalytical Laboratories, work place Spišská Nová Ves, Slovak Republic.

Due to the granularity of the metallurgical sludge on the landfill the content of individual fractions changes locally and the above conclusions may not be valid. The content of dust particles in the individual profiles of the probes varies. There is less dust particles on the surface of the landfill and then to a certain depth below the surface their content increases or locally also decreases as evidenced by the physical analyses of the individual profiles of the probes. This is related to the process of deflation of the dust particles from the landfill surface as well as the shift of clayey and dust particles in relation to the permeability of the sludge into deeper parts of the probes' profiles. This fact is related also to the quality of the ore and its processing (Figure 9).

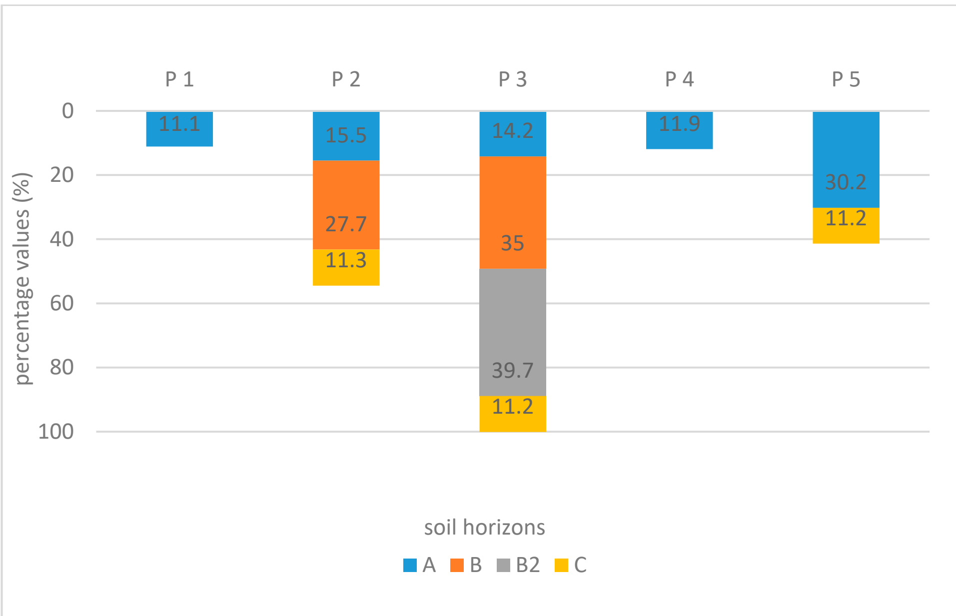

Figure 9. Share of the particles of fraction <0.01 mm in individual horizons of technosols. Legend: probes P1 to P5.

Organisms. We did not carry out research of the fauna in the reclaimed part of the landfill. The results of research from 1982–83 [12] show that the fauna in the landfill consists mainly of dominant and constant species from neighboring geobiocenoses, which have a high tolerance to metallurgical sludge, and occur in the reclaimed part of the landfill. In the rhizosphere we know that resistant organisms are present e.g., wild nematodes aphelenchus avenae and acrobeloides buetschlii, and microscopic mites, arthropods.

4. Discussion

The technosols represent a specific reference group of soils. They are soils whose properties are affected by materials that have a technogenic origin [9]. In the Russian classification system of soils, the terms "technogenic surface formations" or "technogenic surfaces" are used to indicate the technosols [13]. Perhaps the term "technogenic surface" is for some cases more precise than the term "technosols".

The diagnostic materials for the technosols are artefacts. The artefacts are either the artificial materials created by human or the original natural materials that have been partially or completely transformed, e.g., in the process of industrial production or mining. According to the IUSS (International Union of Soil Sciences) working group World Reference Base (WRB) [9] it can also be material transferred to the surface from deep in the Earth through human activity. This material was not affected in the depths of the Earth's crust by the same processes occurring on the Earth's surface. Artefacts are therefore materials that would not occur on the Earth's surface without human activity.

The requirement for identification of technosols is that they must have 20% or more artefacts in the top part of the profile to 100 cm from the surface to the continuous rock [9]. The technosols occur mostly in urbanised and industrial areas in small localities [14]. The development of the profile of technosols is not subject to the natural paedogenesis of a given climate zone.

In the article we discuss the character of technosols that originated in the landfill of metallurgical sludge near the former nickel smelting plant in the industrial part of the town Sered', in an area of approximately 37–40 ha. The sludge has diametrically different properties from the rocks in the natural lowland landscape. The analysis of the sludge samples showed its negative properties in relation to living organisms and their environment. Based on the research of the properties of the sludge, the Research Institute of Experimental Biology and Ecology of the Slovak Academy of Sciences prepared a proposal for the greening of the landfill in 1982/83, mainly due to dangerous secondary dustiness.

The sludge contains 100 times more nickel, 60 times more chromium, and 5 times more manganese than uncontaminated soil. The high content of heavy metals has a toxic effect on plants and this can only be reduced by adding other substrates to the metallurgical sludge and fertilizing. For the elimination of the unfavourable properties of the metallurgical sludge researchers suggested that sludge from the sugar factory was added to the sludge, as well as fertilizer with phosphorus, potassium, and $CaCO_3$ (phosphorus 50–80 kg/ha, potassium 75 kg/ha, and $CaCO_3$ 10 t/ha). This process has improved the properties of the metallurgical sludge. Laboratory experiments have shown that certain types of grass can be sown on sludge treated in this way. The sludge from the sugar factory has pH of 8–11 and the metallurgical sludge is also strongly alkaline. We believe that the addition of the sugar factory sludge was not good solution. This process managed to green only 8 ha of the landfill. The managers of the former nickel smelter stopped the reclamation due to the desire to protect the landfill as it contained secondary raw materials. Access to field research and sampling for analysis was limited by the landfill owners. The trade-off between mining and environmental protection is the only possible starting point for sustainable development in this area.

Thus the profiles of the probes of technosols in the reclaimed part of the landfill are composed from two types of artefacts. The first is the metallurgical sludge and the second is the saturation sludge from the sugar factory. We observed this in the profiles of the exploratory probes No. 2, No. 3, and No. 5 (Figures 10 and 11). In the profile of technosols at the landfill, the volume of artefacts ranges from 90% to 100%. The part of the landfill which is open for mining consists of 100% alkaline metallurgical sludge.

According to the World Reference Base (WRB) for soil resources [9], at the metallurgical sludge of the landfill we identified spolic technosols/alkalic hyperartefactic from the new reference soil group of technosols.

The prefix qualifier of technosols at the metallurgical sludge according to the WRB for soil resources is the spolic. This term refers to technosols, in which industrial technical sediment is located practically from the surface to a depth of more the 100 cm, in our case approximately on 32 ha of landfill area. On 8 ha of the reclaimed part of the landfill the saturating sludge from a sugar factory (pH 8–11) which contained a small amount of organic matter (the beet sugar pulps) and $CaCO_3$ and $MgCO_3$.was added into the metallurgical sludge It is also the technical sediment. The upper part of the profile of the technosols has here a dark-grey colour to a depth of approximately 10–15 cm and a rhizosphere has formed in it. On the landfill platform, where the movement of material was not affected by mass wasting processes the white-grey horizon (Figure 10) was created and sharply demarcated it is located under a 10 cm thick layer of metallurgical sludge. This fact can be explained by the saturation sludge being gradually mechanically shifted from the surface layer of the metallurgical sludge by water over 37 years (despite the fact that area is very dry with a deficit of 150 mm of rainfall per year).

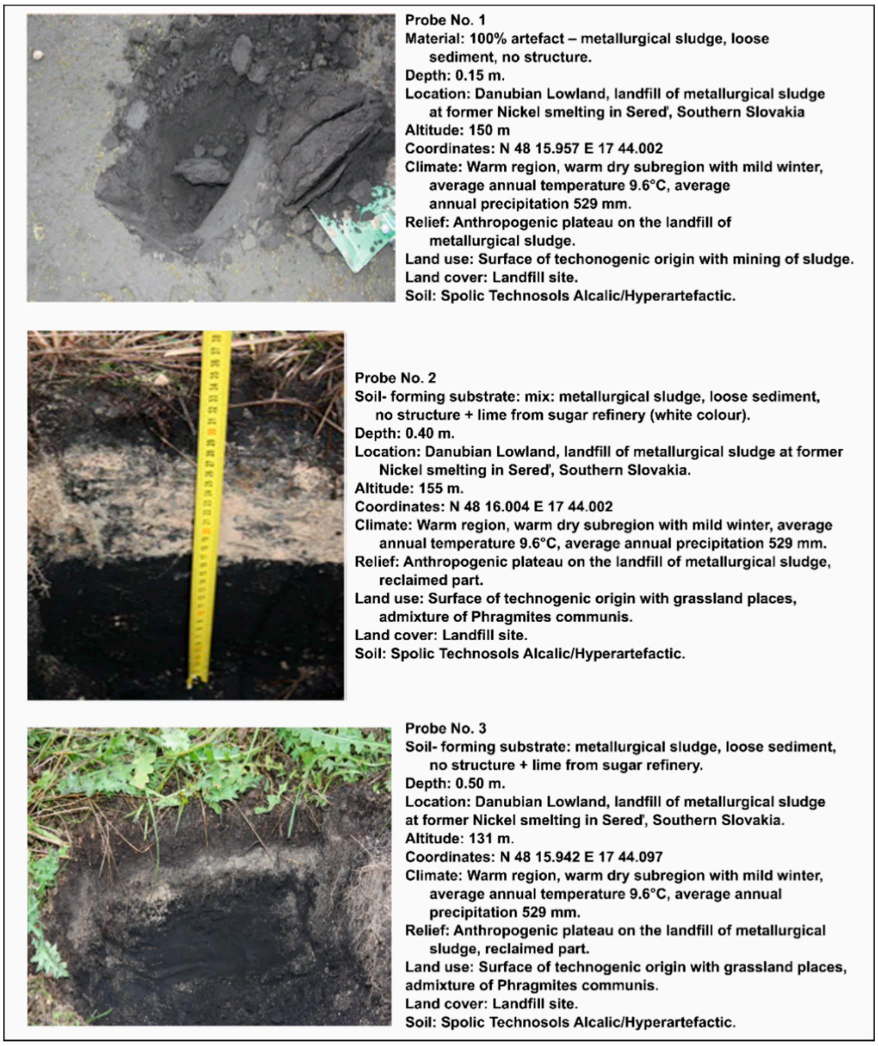

Figure 10. Probes No. 1, 2, and 3 with a description of the parameters of the technosols.

Probe No. 4
Soil-forming substrate: 100% artefact, metallurgical sludge, loose sediment, no structure.
Depth: 0.60 m.
Location: Danubian Lowland, landfill of metallurgical sludge at former nickel smelting plant in Sereď, southern Slovakia.
Altitude: 135 m
Coordinates: N 48 15.927 E 17 43.935
Climate: Warm region, warm dry subregion with mild winter, average annual temperature 9.6°C, average annual precipitation 529 mm.
Relief: Anthropogenic steep slope (45°) on the landfill of metallurgical sludge.
Land use: Surface of techonogenic origin with sludge mining in some places.
Land cover: Landfill site.
Soil: Spolic Technosols Alcalic/Hyperartefactic.

Probe No. 5
Soil-forming substrate: metallurgical sludge, loose sediment, no structure + lime from sugar refinery.
Depth: 0.50 m.
Location: Danubian Lowland, landfill of metallurgical sludge at former nickel smelting in Sereď, southern Slovakia.
Altitude: 131 m.
Coordinates: N 48 15.942 E 17 44.097
Climate: Warm region, warm dry subregion with mild winter, average annual temperature 9.6°C, average annual precipitation 529 mm.
Relief: Anthropogenic plateau on the landfill of metallurgical sludge, reclaimed part.
Land use: Surface of technogenic origin with grassland places, admixture of Phragmites communis.
Land cover: Landfill site.
Soil: Spolic Technosols Alcalic/Hyperartefactic.

Figure 11. Probes No. 4 and 5 with a description of the parameters of the technosols.

The qualifier of the suffix alkalic/hyperatefactic is that the sludge in landfill is alkaline (according the analyses of the samples as strongly alkaline) and composed only of industrial artefacts.

According the results of physical–chemical analyses of the samples from the individual probes we did not identify any soil-forming processes in the profiles at the reclaimed section of the landfill site, which was costly reclaimed 37 years ago.

In the structure of the pedosphere of the landscape of the Danubian Lowland, the technosols (or technogenic surface of the landfill) are ultimately associated via geomorphological processes with neighbouring and more distant soils groups. We can observe the influence of the technogenic surface of the landfill site on the soils around the landfill. During the deflation fine particles of sludge forms dust coatings (Figure 12) on the surface of the arable soils near the landfill and also at a distance of up to 50 km from the landfill site. The metallurgical sludge also settles on vegetation cover, water bodies, and others surfaces.

Figure 12. Dust coatings on the surface of arable soils surrounding the landfill.

5. Conclusions

Attempts to eliminate secondary dustiness from the technogenic surface of a metallurgical sludge landfill took place at two year intervals from 1976 to 1979 and were unsuccessful. The attempt to green the body of the landfill in 1982–83 was partially successful. This attempt however was stopped by the management of the former nickel smelter because of their desire to protect the landfill as a bearer of secondary raw materials. In 1993 production in the nickel plant was terminated for economic reasons, and in 1994 a large landfill became the property of a private company. The landfill has a negative impact on the environment and population health in the following ways:

- With respect to the geographical location, the landfill lies in the agricultural landscape of the Danubian Lowland,
- with respect to the relief, the surface of the landfill body is not stable, and it is subject to fluvial processes on the slopes and to the dangerous process of wind erosion as well as the anthropogenic erosion by the mining, which accelerates all of these processes,
- with respect to the amount of sludge, its toxicity as well as the length of time (57 years) it has been present has induced an impact on the environment and the health of the population,
- critically, the landfill is private property today and entry is only possible with the consent of the owners.

Efforts to improve the environment were manifested by academics rather than the metallurgical plant management and competent authorities. Attempts to eliminate the secondary dustiness of the landfill were unsuccessful, some were absolutely meaningless and ineffective, and those that could have been successful were stopped by the management of the smelter in their desire to protect the landfill as a bearer of secondary raw materials. Stopping the continuous process of sludge deflation, which is currently the most serious problem in the region, especially in terms of population health, is possible only on the basis of research of the landform of the landfill and detailed research of the physical and chemical properties of metallurgical sludge, which will show the way to remediation of the landfill. It is unacceptable that chromium and other heavy metals have been carried into the air by deflation from the landfill for more than half a century. The only possible solution to the problem today is the stoppage of mining and the remediation of the landfill by greening.

As our research showed, reclamation on the landfill platform (the landfill was not reclaimed in its entirety) was partially successful. The landfill slopes could not be reclaimed due to geomorphological processes. In the rest of the landfill, ongoing mining accelerates the transfer of materials by deflation to a distance of up to 50 km. Rainfall, which causes material to seep into the Váh River, also contributes to the transmission of pollution. Emissions containing metals, especially chromium, are transported to the surrounding settlements posing a serious health risk to the region's population, and a compromise must be found between mining and environmental protection in the future in terms of sustainable development.

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References

1. Kalebáč, O.; Soušek, V.; Had, A. Výroba chrómového surového železa z loužencového aglomerátu. *Hutnícke Listy* **1987**, *10*, 705–711.
2. Michaeli, E.; Boltižiar, M.; Ivanová, M. Geoecological structure of the dump of technological waste (Fe-concentrate) et Sereď. *Acta Fac. Studiorum Humanit. Nat. Univ. Prešoviensis Folia Geographica.* **2009**, *XLIX*, 180–197.
3. Mičian, L'. Vplyv geomorfologických pomerov na charakter pôdneho krytu. *Acta Geol. Geogr.* **1965**, *5*, 16–120.
4. Maglay, J.; Pristaš, J.; Nagy, A. *Vysvetlivky ku Geologickej Mape Podunajskej Nížiny-Trnavskej Pahorkatiny v Mierke: 1: 50 000*; ŠGÚDŠ: Bratislava, Slovakia, 2005.
5. Lewis, S.L.; Maslin, M.A. Defining the Anthropocene. *Nature* **2015**, *519*, 171–180. [CrossRef] [PubMed]
6. Zapletal, L. Geneticko-morfologická klasifikace antropogenních forem reliéfu. *Acta Univ. Palacki. Olomuc. Geogr. Geol.* **1968**, *VIII*, 239–427.
7. Lacika, J. *Antropogénna Transformácia Reliéfu Ako Indikátor Trvalej Udržatel'nosti*; FPV UMB: Banská Bystrica, Slovakia, 1999; ISBN 80-8055-471-4.
8. Lapin, M.; Faško, P.; Melo, M.; Štasný, P.; Tomlain, J. Climatic regions. In *Landscape atlas of the Slovak Republic*, 1st ed.; Institute of Landscape Ecology of the Slovak Academy of Sciences Bratislava: Bratislava, Slovakia, 2002; p. 344.
9. World Reference Base for Soil Resources. *International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*; FAO: Rome, Italy, 2015.
10. Jurko, A. *Ekologické a Socioekonomické Hodnotenie Vegetácie*; Vydavatel'stvo Príroda: Bratislava, Slovakia, 1990; ISBN 80-07-00391-6.
11. Sobocká, J.; Poltárska, K. Description of technogenic spoil bank and its influence on agricultural soils. (A case of nickel metallurgy refuse at Sered'). *Ved. Práce VUPOP* **2004**, 103–112.
12. Paulech, C.; Šály, A. Základný biologicko-ekologický prieskum v oblasti haldy lúženca v Niklovej hute v Seredi. In *Záverečná Správa Ústav Experimentálnej Biológie a Ekológia SAV*; Ústav experimentálnej biológie a ekológie SAV: Bratislava, Slovakia, 1983; pp. 8–24.
13. Shishov, L.L.; Tonkonogov, V.D.; Lebedeva, I.I.; Gerasimova, M.I. *Russian Soil Classification System*; World Reference Base for Soil Resources 2015; Dokuchaev Soil Science Institute: Moscow, Russia, 2001.
14. Schad, P. Technosols in the World Reference Base for Soil Resources-history and definitions. *J. Soil Sci. Plant Nutr.* **2018**, *64*, 138–144. [CrossRef]