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Improving the Content of Chemical Elements from the Soil of Waste Heaps Influenced by Forest Vegetation—A Case Study of Moldova Nouă Waste Heaps, South-West Romania

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Abstract: The present article emphasizes the influence of forest vegetation on improving the content of toxic elements from soil, increasing the content of micro and macro elements as well as correlating these variations with characteristics of forest vegetation from the studied areas—Moldova Nouă waste heaps, South-West Romania. The research involved comparing and observing the differences in the content of micro, macro, and toxic elements (Fe, Pb, Zn, and Cd) between the soil of waste heaps from Moldova Nouă from areas with forest vegetation and the content of these elements analyzed 31 years ago during the projection of afforestation works, when forest vegetation was missing. The differences were correlated with stand characteristics of forest vegetation. We observed a significant increase for Fe and a significant decrease for Zn and Cd. The influence of forest vegetation of the variation on the soil's chemical composition was studied for the chemical elements that previously showed significant differences (Fe, Zn, and Cd). The averages of the statistically significant differences for the concentration of each analyzed element (Fe, Zn, and Cd) were correlated with the characteristics of the stands from the studied sampling points. The variation in time for Fe, Zn, and Cd and actual content of P, Cu, Mg were correlated especially with the average height of trees.

Keywords: forest plantations; heavy metals; mining sterile; copper ore; soil elements; stand characteristics

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1. Introduction

Mining is an important industry, representing 6.9% of the global PIB, being well studied in the specialty literature [1]. Moldova Nouă, the sterile on which forest plantations were created, is a covering technosoil that resulted from processing the local granodiorites (banatites) [2]. The used waters resulting from flotation were transported to decanting ponds, where they were settled, resulting in a sterile in the form of heaps, laid down in horizontal overlaid layers. Considerable discharge differences were present in its solid and liquid state [2]. They consisted of the product's chemical reaction (pH 8.05–11.35 for water, compared with 7.5–7.8 for sand), as well as its chemical composition [3].

In many parts of the world, mining activities performed in the past have left significant amounts of sterile material improperly deposited. Sterile materials contain high levels of heavy metals that contaminate soil substrates, destroying their texture and causing groundwater pollution and a decline in biological diversity [4]. Waste generated by mining activity poses a serious issue due to its large amount, being often associated with risks posed by its storage for environmental management [5]. From these formed waste heaps, high concentrations of potentially toxic elements can spread on arable fields and meadows nearby, leading to heavy metal pollution. Acid drainage and eolian dust transportation are the main causes of pollution dispersion. In some cases, acid drainage from mine waste dumps can be partly responsible for relatively high acidity (pH < 5.0) measured in samples collected from arable land and pastures [6]. Solid metal compounds can deposit at a distance of up to a few km [7]. Regarding flood transportation of pollution, another important cause of pollution dispersion is proven by the fact that the direction of flow of surface water on the slopes explains the downstream spread of pollution in some studied areas in other research [6]. Geochemical transformations of the mineral content from waste heaps can significantly impact the soil's chemical properties [8,9]. Some investigations have shown that sterile samples have an extremely variable content of potentially toxic elements (Cu, Pb, Zn, Bi, Cd, and As) [10]. This highlights the necessity to phytoremedy the areas polluted in this way as fast as possible.

Heavy metals pollute soil and water resources, being harmful to human health [11,12]. Some toxic elements at high concentrations can inhibit plant growth [13]. In order to obtain lasting development, mining areas are restored, with this being an important phase of mining activities [14]. In order to fight against the negative effects of pollution, some investigations have demonstrated the feasibility of using black locust (*Robinia pseudoacacia* L.) in the phytoremedy of waste heaps [15]. Currently, there are numerous restoration solutions, but the most important one remains afforestation, considered the most friendly towards the environment [16].

Statistical analysis of the chemical fluctuations of Pb, Zn, Cu, As, and Mn concentrations has shown that the highest concentrations of heavy metals are usually found on the waste heap's central plateau [17]. As such, the solution used in Moldova Nouă to afforest the waste heaps' perimeter as well as add forest belts inside them is optimum in regard to hindering wind wrecking of the sterile located inside the waste heaps (this being the most concentrated in heavy metals). Afforestation works conducted on waste heaps from Moldova Nouă had the purpose of reducing pollution from waste heap dust crumbled by the wind. Different pioneering species were used, such as black locust (*Robinia pseudoacacia* L.), oleaster (*Elaeagnus angustifolia* L.), sea buckthorn (*Hippophaë rhamnoides* L.), black cherry (*Prunus serotina* Ehrh.), shaky poplar (*Populus tremula* L.), etc. Besides reducing dust pollution, these methods can also improve the soil's microbiological diversity [18], the diversity of the planted species, and the different degrees of decomposition of the dead wood. At the same time, they influence the soil's respiration rate and diversify the environmental conditions of the soil [19].

The purpose of the investigations conducted in the present article was to emphasize the influence of forest vegetation on improving the content of potentially toxic elements from the soil, to increase the content of micro and macro elements, and to correlate these variations with the characteristics of the forest vegetation from the studied areas. The context indicates a decrease in the percentage of these heavy metals, as well as other soil compounds that were levigated or absorbed at the tree's radicular level, followed by a decrease in specific soil chemical processes.

The purpose of the investigation was obtained by fulfilling the following specific objectives:

- Comparing the chemical composition of the sterile before planting with the chemical composition of the soil from forest plantations;
- Analyzing the variation of the soil's chemical composition from forest plantations located on waste heaps;
- Establishing the influence of forest vegetation on the variation of the soil's chemical composition in forest plantations located on waste heaps.

This study's hypothesis is based on previously conducted investigations on waste heap plantations from Moldova Nouă, which led to the observation of sustained growth of the forest vegetation planted there. Taking into account this aspect, as well as the accumulation of wood mass, this study's hypothesis is that the content of potentially toxic elements from the soil of waste heaps is improved under the influence of forest vegetation.

Our research involved comparing the content of micro, macro, and potentially toxic elements from the soils of waste heaps present in Moldova Nouă, from areas with forest vegetation, with their content determined by analyzing the sterile 31 years ago during afforestation projection works. The observed differences were correlated with the different characteristics of stands planted on waste heaps.

2. Materials and Methods

2.1. Study Area

Important reserves of copper ore from the city of Moldova Nouă, in southwestern Romania (Figure 1), have caused mining exploitations with the purpose of obtaining copper concentrates. The objectives of mining exploitations have covered a large area which included especially subterranean and surface extraction activities, as well as preparing these ores. The final result was a copper concentrate of 15–18%, a pyrite concentrate of 40–45% sulfur, and a very large quantity of sterile [2]. The flotation of ores from Moldova Nouă was obtained using collective–selective technology, resulting in a copper concentrate (15–18% Cu) and a pyrite concentrate (40–43% S). The final sterile was conducted through magnetic separators, before being transported to the decanting pond. Once deposited on the waste heap, these substances changed the sand's reactivity and chemistry, contributing to its cementation and stratification.

In the above topographical figure, sampling areas where samples were harvested in 1988 include the sampling points where sampling were harvested in 2019. Due to technical limitations for the exact positioning of sample points in 1988, it cannot be said that their positioning is known, for which reason, we preferred that the sampling in 1988 be expressed as the sampling area and not as the sampling point.

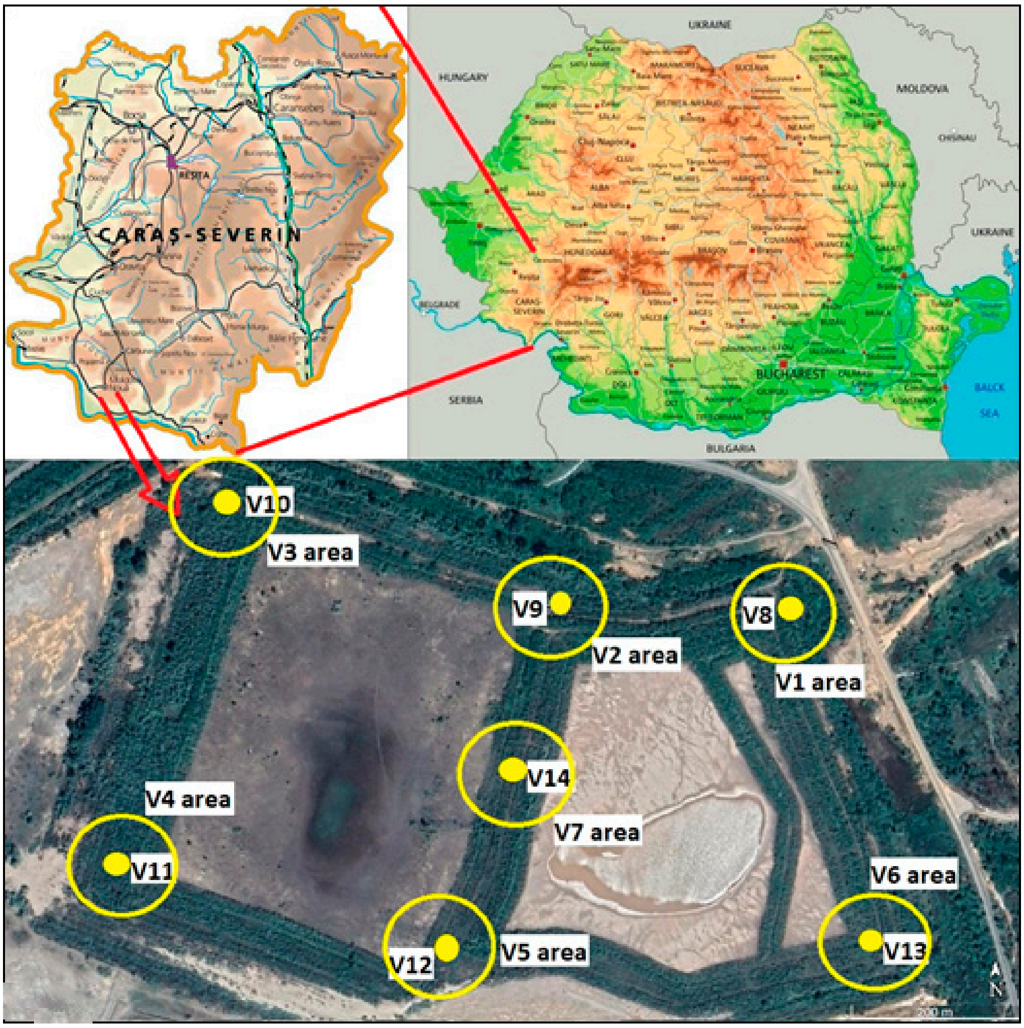


Figure 1. The location of the analyzed sampling points within forest plantations from the waste heaps located in Moldova Nouă, Caraş-Severin county, southwestern Romania: V1–V7, the area where soil analyses were performed in 1988 (yellow circles); V8–V14, the sampling points where soil analyses were performed in 2019 (yellow points) [20–22].

Over 40 years of mining activity in Moldova Nouă have led to the accumulation of large waste deposits on the Danube river's left bank, near Romanian cities (Moldova Veche and Coronini) and Serbian cities (Golubat). The average monthly volume of this sterile deposited in the decantation ponds (waste heaps) reached approximately 140,000 tones during the peak functioning of mining activity and covered a surface of approximately 130 ha. The annual increasing rhythm was over 5 ha, while its granulometric composition consisted of sand (85–95%), dust (4.1–9.3%), clay (1.4–9.7%), and humus (1.1–2.8%), with a slightly basic pH, varying between 7.5 and 7.8, explained by the calcareous nature of the mining rocks [23].

In the study area, in addition to the analyzed soil and tailings, research materials are also represented by the forest plantations made in 1988 on the tailing dumps. As a type of vegetation, forest vegetation was used. The woody perennials were planted on forest belts, on the slope, and on the edges of tailing dumps. Different pioneering species were used, such as black locust, oleaster, sea buckthorn, black cherry, shaky poplar, etc.

2.2. Experimental Section

The research was conducted in Moldova Nouă, one of the most important copper extraction centers in Romania. The research was concuted at 14 sampling points (V1–V14) where we analyzed the soil's chemical composition and determined some stand characteristics.

Soil samples were gathered from sample points from the corners and middle of the waste heap proposed at that time for afforestation where soil samples were gathered (V1–V7, 1988) and sample points at the same location were established (V8–V14, 2019), whose coordinates were found using old maps of the waste dump overlaid on satellite imagery and identified in the field using GPS.

Soil analyses conducted in 1988 on waste heaps without forest vegetation were performed in the V1–V7 sampling points. Soil samples were gathered from the corners of the waste heap proposed at that time for afforestation, as well as from the middle of the heap's large sides and from the central part of the plateau. Through these points, a forest belt was projected. Its purpose was to split the surface occupied by the sterile from the waste heap's interior, and to stop deflation and the spreading of sterile by the wind (Figure 1).

The V8–V14 sampling points were located at approximately the same locations from 1988, as shown above (Figure 1). Soil samples from them, namely from the afforested areas of the waste heap, were analyzed in 2019. In addition, measurements of forest vegetation were conducted. The results of the soil analysis were compared with the results of the analysis obtained in 1988. Today, due to forest plantations, the perimeter of the waste heaps and forest belts from the inside are covered by true forests of mixed pioneering species.

2.3. Sample Prelevation and Element Detection

Both sets of soil samples, from 2019 and 1988, were gathered from depths between 25 cm and 40 cm, based on the possibility of penetrating the soil. Soil sampling was conducted according to ISO 18400-104:2018—Soil quality—Sampling—Part 104: Strategies, using an auger soil sampler [24]. The sterile samples from 1988 were gathered according to the usual pedological methodology and were analyzed at the Pedology laboratory at the Forestry Research and Management Institute in Bucharest (the present Silviculture Research and Development National Institute). The micro elements (Fe and Zn) and potentially toxic elements (Pb, Cd, V, and Ra) were determined through atomic absorption spectrometry, the same method used for the analyses from 2019, but applied by a different laboratory, using equipments sourced from Varian Inc., Victoria, Australia. Because of unmaterialized sampling points in the open field without forest vegetation in 1988 and without knowing the sampling points' coordinates, but knowing just the area of the sampling points at that time in accordance with the afforestation project (the corners of the waste heap, the middle of the heap's large sides, and the central part of the plateau—yellow circles in Figure 1) the analysis from 2019 was not a perfect replication of the analysis from 1988 in terms of the sampling points but only with regard to the sampling area.

The soil samples gathered in 2019 were analyzed in the laboratory at the "Regele Mihai I" Life Sciences University, Timişoara. For these analyses, a macro and micro elements analysis was conducted according to SR EN 14082/2003 [25]. As such, 3 g of samples were burned for calcination at 650 °C for 8 h (until a light grey ash was obtained) in a Nabertherm B150 oven, sourced from Nabertherm GmbH, Lilienthal, Germany. The resulting ash, dissolved in 20% HCI, was transferred with a final volume of 20 mL. The elements (Ca, K, P, Mg, Cu, Fe, Zn, Cr, Ni, Mn, Cr, Pb, and Cd) were determined through atomic absorption spectroscopy, by using the Varian 220 FAA equipment, sourced from Varian Inc., Victoria, Australia. The detection limits (DML) for the analyzed elements were 0.02 ppm for K and Mg, 0.06 ppm for Cu, Mn, Fe, Zn, and 0.03 ppm for Ca. In order to make the analysis estimate as accurate as possible, each sample collected from the sample points was divided in the laboratory into three sub-samples, which were separately analyzed. The initial results of the analysis represented the total content for each element and were expressed in ppm, reported to the weight of the fresh sample. In the analyses, the average determination of the three sub-samples was included, except for the content variation of the element figure representation, where the average of all 21 sub-samples was used.

In order to equate and compare with the results from 1988, the 2019 sample results were expressed in calculations as a percentage of the total. The transformation from parts per million to percentages was performed for each individual sample. This was not expressed (neither in the case of the samples from 1988 nor in the case of those from 2019) in the weight of each individual element and their sum does not summarize up to 100%. Each element was expressed as a percentage of the total mass of the sample. Thus, the sum of the percentages of the determined elements varied in the 8 samples from 2019 between 12% and 49%, the rest up to 100% being undetermined inert material. In the samples from 1988, the sum of the percentages of the determined elements varied between 35% and 56%. All chemical substances and solvents used in this study were of an analytic degree. The atomic absorption spectrophotometric method was used in analyzing both sets of samples (from 1988 and 2019).

2.4. Trees Measurements

The seven points from which samples were gathered in 2019 belong to a research device in which seven circular sample surfaces of 100 m^2 each were previously created. All trees from these samples were inventoried. Their measurements targeted biometric characteristics (height and diameter at 1.3 m), as well as the species composition of stands installed there. For them, a tree caliper was used in order to measure diameters, followed by the VERTEX equipment for determining tree heights, sourced from Haglöf Sweden AB, Hamre, Sweden. The VERTEX equipment was also used for confining sample surfaces. The stand composition from the studied surfaces was determined as a participation percentage of each species identified in the sample surface.

The volume of trees from each sample surface was calculated using the following formula [26]:

$$\log V = a_0 + a_1 \log d + a_2 \log^2 d + a_3 \log h + a_4 \log^2 h$$

where

a_1, a_2, a_3, a_4 are the values of regression coefficients of the species;
d is the tree diameter [cm];
h is the tree height [m];
V is the tree volume [m^3].

2.5. Statistical Analysis

The testing of the differences between the average values of the micro, macro, and potentially toxic elements content from the waste heap's soil was conducted for the commonly analyzed elements (Fe, Pb, Zn, Cd, and Ca) in 1988 and 2019, using an ANOVA statistical test. For these elements, we calculated the average of the analyzed samples, the standard deviation, and the variation coefficient. The ANOVA statistical test was used to test the hypothesis that significant differences between the concentration of different macro, micro, and potentially toxic elements from the waste heap's soil existed before the installation of forest vegetation compared with their current concentration.

The testing of the significance of differences on the sampling points was performed with a t-Student statistical test for the soil elements, for which the ANOVA statistical test emphasized significant differences between the average values. By using a Two-Sample Assuming Unequal Variances t-test with Two-tail for testing statistically the differences between sampling points regarding the content of soil elements, we compared the results of the soil analysis from 2019 at the 7 sampling points from Moldova Nouă waste heaps (V8–V14) with the sterile analysis realized more than 30 years ago (V1–V7). p-values obtained from the t-test were adjusted by the "False Discovery Rate" (FDR) using the Benjamini–Hochberg method.

Furthermore, for the elements for which the t-test adjusted by the FDR emphasized significant differences between the average values from 1988 and 2019, we created linear models regarding the improvement of soil concentration of these elements as follows: Pattern no. 1—Growth of Fe content and Pattern no. 2—Decrease in Cd content. The fitting of the obtained models was tested using χ^2 for goodness of fit.

Before analyzing the influence of forest vegetation on the soil's chemical composition, we used the Shapiro–Wilk and Kolmogorov–Smirnov statistical tests for testing the normality of the distribution of tree numbers in the sample surfaces, and the normality of the average values of the measured biometric characteristics (height and diameter).

We determined the average of differences regarding the Fe, Zn, and Cd concentrations of the statistically significant concentrations from V1 to V7, compared individually with those from V8 to V14 where the tree's biometric characteristics were measured.

A Pearson correlation and PCA analysis were conducted on the tree's biometric characteristics in the sample surfaces and the elements for which the ANOVA test identified significant statistical differences regarding the concentration of elements from 1988 and 2019. In the same way, we analyzed the correlation between the macro elements, micro elements, and potentially toxic elements whose content in the waste heap's soil was analyzed exclusively in 2019.

2.6. Experimental Design

The experimental design of the works as well as the work process in the field stage and data processing are presented in Figure 2.

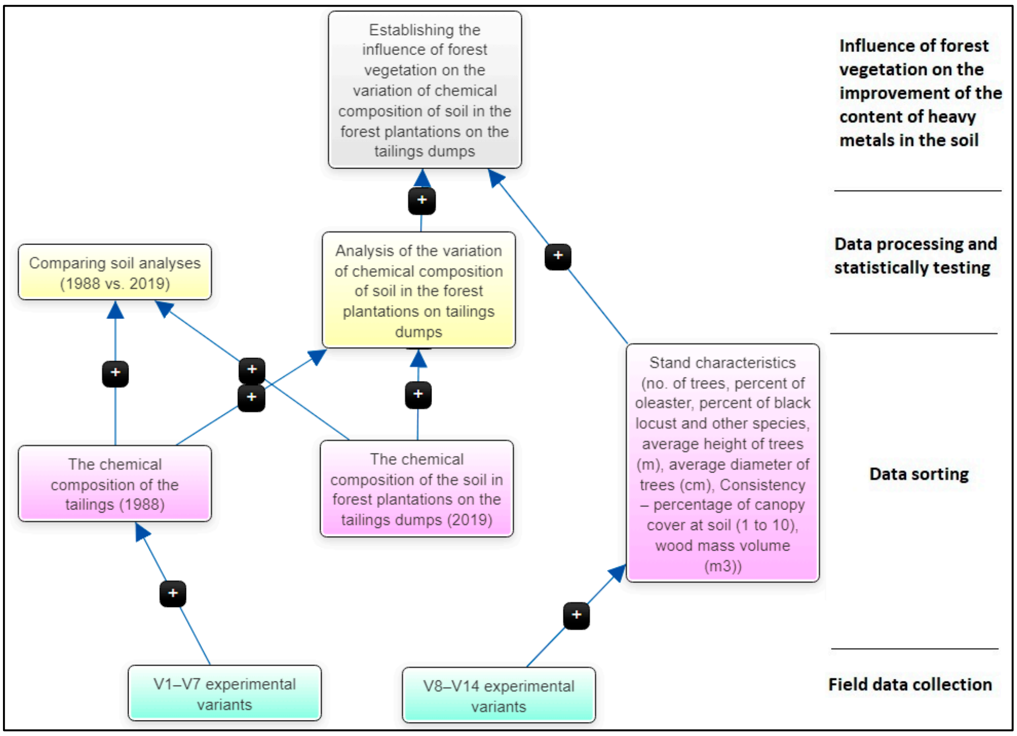


Figure 2. The design of the realized methods and the work flux (using mentalmodeller.org) (the tasks in the figure are colored according to work flows from the right side).

3. Results

3.1. The Chemical Composition of the Sterile before Planting (1988) and of the Soil from Forest Plantations (2019)

The sterile ore contains high quantities of sulfates (150 mg/dm^3), chloride (67.4 mg/dm^3), calcium (135 mg/dm^3), sodium (43 mc/dm^3), and potassium (10.5 mg/dm^3), completed by small quantities (0.04–0.16 mg/dm^3) of magnesium, lead, copper, iron, manganese, and very rarely, phenols.

As for the soil's chemical composition (sand), we can see the predominance of SiO_2 (31.82%) and CaO (15%). Fe (5.33%) and S (1.48%) are present in average quantities, while heavy metals, rare metals, and Al_2O_3 are in small quantities (under 1%). All the other compounds are weakly represented or appear only as marks (Table 1). In the sampling points where some compounds appear only as marks, the compounds are below the limit of quantification. For calculation, their percentage participation is mathematically expressed numerically through 10^{-99}.

The analysis conducted in 2019 (Table 2) with the purpose of evaluating the current chemical composition of the waste heap's soil and comparing the results with the ones realized 31 years ago, shows a composition decrease in some potentially toxic elements such as Cd and Pb. A data comparison was conducted for common elements from both sets (1988 and 2019) of chemical analyses (Fe, Pb, Zn, Cd, and CaO).

After the analysis, we observed an increase in the concentration of some micro elements, such as Fe, as well as some macro elements, such as Ca. All other micro and potentially toxic elements are in a very low percentage (<1%), with the exception of Mg (1.16%).

Potentially toxic elements such as V and Ra identified in some samples analyzed in 1988 were not identified in the analyses conducted in 2019. These recent analyses intended to determine some macro elements, such as P, K, and Mg, as well as some heavy metals, such as Cu, which was not determined in the 1988 analyses but whose presence was evident, taking into account the exploited Cu deposit.

Table 1. The chemical composition of sand from waste heaps (1988).

Sampling Point	Chemical Elements, wt.% of Total										
	Fe	**S**	**V**	**Pb**	**Zn**	**Cd**	**Ra**	**CaO**	**SiO_2**	**Al_2O_3**	**TIO_2**
V1	7.230	2.260	0.0170	0.100	0.090	0.001	0.104	20	31.310	0.0	0.150
V2	5.470	1.790	0.030	0.100	0.050	0.010	0.0	24	31.560	0.0	0.230
V3	5.560	3.800	0.0	0.0	0.120	0.010	0.100	18	33.750	0.0	0.770
V4	6.400	0.450	0.020	marks	0.010	0.001	0.002	15	32.650	0.0	0.370
V5	3.830	0.610	0.020	0.010	0.060	marks	0.003	24	32.700	0.0	0.310
V6	4.400	0.710	0.0	0.001	0.060	0.010	0.0	4	30.390	0.0	0.240
V7	4.400	0.710	0.0	0.0	0.0	0.0	0.0	0	30.390	4.320	0.240
Average	5.327	1.478	0.012	0.030	0.056	0.005	0.029	15	31.821	0.617	0.330

Table 2. The chemical composition of soil from waste heaps (2019).

Sampling Point	Chemical Elements, as wt.% of Total											
	P_{AL} *	**K_{AL} ***	**Cu**	**Cd**	**Cr**	**Ni**	**Pb**	**Zn**	**Fe**	**Mn**	**CaO**	**Mg**
V8	0.00101	0.015	0.063	0.00021	0.0013	0.0016	0.0057	0.015	8.594	0.048	2.019	1.037
V9	0.00004	0.026	0.056	0.00020	0.0025	0.0028	0.0025	0.017	8.217	0.060	29.557	1.187
V10	0.00002	0.027	0.063	0.00024	0.0017	0.0019	0.0029	0.017	9.706	0.077	37.248	1.499
V11	0.00014	0.034	0.048	0.00014	0.0022	0.0025	0.0065	0.016	6.629	0.072	25.207	1.225
V12	0.00130	0.036	0.021	0.00005	0.0032	0.0036	0.0046	0.012	5.137	0.063	7.825	0.988
V13	0.00042	0.022	0.0690	0.00022	0.0023	0.0026	0.0034	0.016	7.893	0.053	14.506	1.219
V14	0.00002	0.007	0.083	0.00040	0.0016	0.0015	0.0070	0.019	9.617	0.043	21.117	0.998
Average	0.00042	0.0240	0.058	0.00021	0.0021	0.0023	0.0046	0.016	7.970	0.059	19.640	1.165

* P_{AL} and K_{AL} are P and K extracted in ammonium acetate lactate—forms from soil accessible to plants.

3.2. The Variation of the Soil's Chemical Compositions in Forest Plantations from Waste Heaps

The variation of the soil's chemical composition in forest plantations from Moldova Nouă waste heaps between 1988 and 2019 was analyzed for the Pb and Cd potentially toxic elements, for the Fe and Zn micro elements, and for the CaO macro elements (Table 3).

Table 3. Average values of some of the macro, micro, and potentially toxic elements from the waste heaps' soil in 1988 and 2019, and *p* values (ANOVA test) for testing differences in concentrations of elements between 1988 and 2019 (significant ($p < 0.05$) = *; distinct significant ($p < 0.01$) = **).

Macro elements, Micro elements, and Potentially Toxic Elements	1998			2019			*p* Values (ANOVA Test) for Testing Differences in Concentrations of Elements between 1988 and 2019
	Average (% from Total)	Standard Deviation	Variation Coefficient	Average (% from Total)	Standard Deviation	Variation Coefficient	
Fe	5.328	1.212	0.227	7.970	1.633	0.205	0.005 **
Pb	0.030	0.048	1.588	0.005	0.002	0.385	0.184
Zn	0.056	0.002	0.133	0.016	0.042	0.753	0.028 *
Cd	0.005	0.005	1.114	0.0002	0.0001	0.519	0.043 *
CaO	15.000	9.504	0.634	19.640	12.369	0.630	0.447

The values of the variation coefficient calculated for the concentration of elements from the analyzed samples show a homogeneity in the time of concentrations for different elements. We can observe a leveling of potentially toxic element concentrations, given especially by the decrease in their concentration in different areas of the waste heap.

By testing differences in the concentration of elements between 1988 and 2019, we can observe distinct significant differences in Fe concentration ($p < 1\%$) and significant differences in Zn and Cd concentrations ($p < 5\%$). No significant differences are observed for Pb and CaO between the analyzed samples.

By testing Fe concentration differences, we can see significantly distinct and very significant growths in most pairs of analyzed samplings (Table 4).

Fe growths with statistical significance (*—significant; **—distinct significant; ***—very significant) were recorded in most sampling pairs, with the exception of V2–V12, V3–V12, and V4–V11.

As can be seen in Figure 3, the average Fe content among all 21 analyzed sub-samples (each sample was tripled in the laboratory for analyses) from the waste heaps' soil (tested above with an ANOVA—Table 3) grows during the studied period.

Significant decreases in the Zn content were recorded by comparing their content from sampling points V1, V3, and V5 with the content from sampling points from 2019 (V8–V14) and between V7 and V8 (Two-Sample Assuming Unequal Variances t-test with Two-tail). After adjusting the "False Discovery Rate" using the Benjamini–Hochberg method, it was proven that there is no statistical significance regarding the differences in Zn concentration in the soil between 2019 and 1988 for any of the significance thresholds, with the adjusted values of *p* in all cases being greater than 0.05. As for Cd, if we compare the samplings analyzed in 1988 with the ones analyzed in 2019, we can see important and significant decreases from a statistical perspective, as well as increases, but in a quantum significantly lower than the decreases (Table 5). Significant statistical decreases were emphasized between V2, V3, V4, and V6 sampling points (1988) and most samplings that were analyzed in 2019. Statistically significant reduced growths were determined by comparing the Cd concentration from V5 and V7 with most of the samplings from 2019.

Table 4. *p* values (Two-Sample Assuming Unequal Variances t-test with Two-tail) adjusted by the "False Discovery Rate" (Benjamini–Hochberg method) for testing Fe concentration differences between 1988 and 2019 (significant ($p < 0.05$) = *; distinct significant ($p < 0.01$) = **; very significant ($p < 0.001\%$) = ***) and differences between tested values in pairs of variants.

***p* Values between Pairs of Tested Values of Sampling Points/ Differences between Tested Values in Pairs of Samplings (%)—2019 (V8–V14) and 1988 (V1–V7)**							
Sampling point and Fe percentage	V8 (8.5940)	V9 (8.2165)	V10 (9.7062)	V11 (6.6290)	V12 (5.1370)	V13 (7.8926)	V14 (9.6169)
V1 (7.230)	0.01038 */ 1.364	0.00777 **/ 0.986	0.00062 ***/ 2.476	0.02727 */ −0.601	0.00089 ***/ −2.093	0.02216 */ 0.663	0.00152 **/ 2.387
V2 (5.470)	0.0019 **/ 3.124	0.00031 ***/ 2.747	0.00031 ***/ 4.236	0.00252 **/ 1.159	0.13455/ −0.333	0.00048 ***/ 2.423	0.0007 ***/ 4.147
V3 (5.560)	0.00272 **/ 3.034	0.00025 ***/ 2.657	0.00048 ***/ 4.146	0.00331 **/ 1.069	0.0785/ −0.423	0.00061 ***/ 2.333	0.00118 ***/ 4.057
V4 (6.400)	0.00747 **/ 2.194	0.00031 ***/ 1.817	0.00103 **/ 3.306	0.1718/ 0.229	0.00747 **/ −1.263	0.00266 **/ 1.493	0.00259 **/ 3.217
V5 (3.803)	0.0019 **/ 4.764	0.000065 ***/ 4.387	0.00061 ***/ 5.876	0.0007 ***/ 2.799	0.00747 **/ 1.307	0.00061 ***/ 4.063	0.00117 **/ 5.787
V6 (4.400)	0.00152 **/ 4.194	0.000065 ***/ 3.817	0.00306 **/ 5.306	0.00061 ***/ 2.229	0.0209 */ 0.737	0.00038 ***/ 3.493	0.0007 ***/ 5.217
V7 (4.400)	0.00252 **/ 4.194	0.000065 ***/ 3.817	0.000613 ***/ 5.306	0.00132 **/ 2.229	0.0272 */ 0.737	0.0007 ***/ 3.493	0.00145 **/ 5.217

Table 5. *p* values (Two-Sample Assuming Unequal Variances t-test with Two-tail) adjusted by "False Discovery Rate" (Benjamini–Hochberg method) for testing Cd concentration differences between 1988 and 2019 (significant ($p < 0.05$) = *; distinct significant ($p < 0.01$) = **; very significant ($p < 0.001$) = ***) and differences between tested values in samplings pairs.

***p* Values between Pairs of Tested Values on Sampling Points/ Differences between Tested Values in Pairs of Samplings (%)—2019 (V8–V14) and 1988 (V1–V7)**							
Sampling point and *Cd* percentage	V8 (0.0002129)	V9 (0.0001985)	V10 (0.0002427)	V11 (0.0001383)	V12 (0.0000484)	V13 (0.000222)	V14 (0.00021)
V1 (0.001)	0.2710/ −0.0008	0.2710/ −0.0008	0.2746/ −0.0008	0.2528/ −0.0009	0.2247/ −0.0010	0.2710/ −0.0008	0.3570/ −0.0006
V2 (0.010)	0.0059 **/ −0.0098	0.0059 **/ −0.0098	0.0059 **/ −00098	0.0059 **/ −0.0099	0.0059 **/ −0.0100	0.0059 **/ −0.0098	0.0059 **/ −0.0096
V3 (0.010)	0.0059 **/ −0.0098	0.0059 **/ −0.0098	0.0059 **/ −0.0098	0.0059 **/ −0.0099	0.0059 **/ −0.0100	0.0059 **/ −0.0098	0.0059 **/ −0.0096
V4 (0.001)	0.0585/ −0.0008	0.0585/ −0.0008	0.0594/ −0.0008	0.0532/ −0.0009	0.0442 */ −0.0010	0.0593/ −0.0008	0.0909/ −0.0006
V5 (marks)	0.0074 **/ 0.0002	0.0056 **/ 0.0002	0.0074 **/ 0.0002	0.0056 **/ 0.0001	0.1099/ 0.0000	0.0056 ***/ 0.0002	0.0056 **/ 0.0004
V6 (0.010)	0.0056 **/ −0.0098	0.0056 **/ −0.0098	0.0056 **/ −0.0098	0.0056 **/ −0.0099	0.0056 **/ −0.0100	0.0056 **/ −0.0098	0.0056 **/ −0.0096
V7 (0.0)	0.0074 **/ 0.0002	0.0056 **/ 0.0002	0.0074 **/ 0.0002	0.0056 **/ 0.0001	0.1099/ 0.0000	0.0056 ***/ 0.0002	0.0056 **/ 0.0004

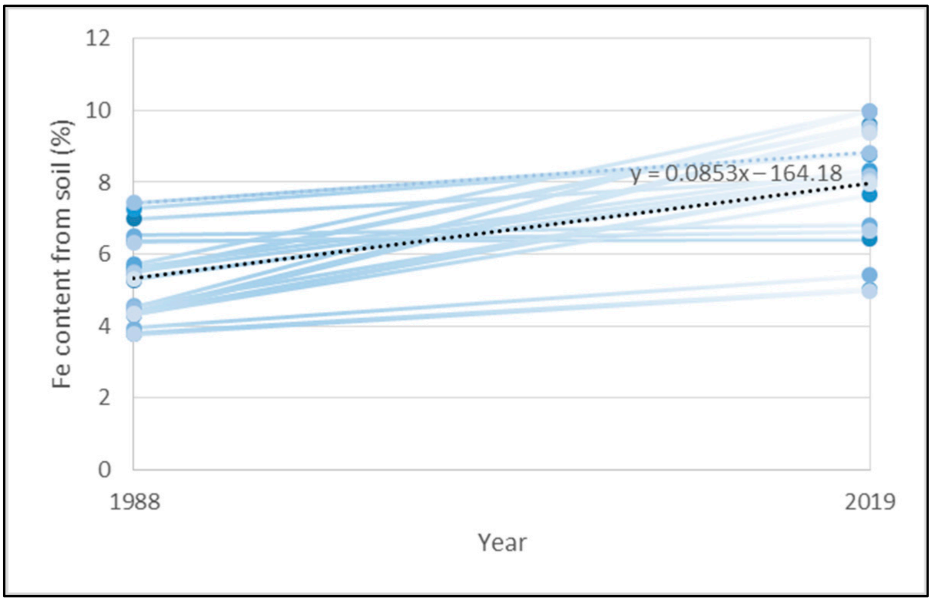


Figure 3. Growth of Fe content (%) from Moldova Nouă waste heaps' soil during 1988–2019 (Pattern no. 1; color lines express the correspondence between analysed samples in 1988 and 2019).

Cd had a strong decrease in the average of analyzed sub-samples (three for each sampling point) content from the waste heaps' soil (Table 5, Figure 4) especially in V2, V3, and V6, where the concentration of this potentially toxic element was very high.

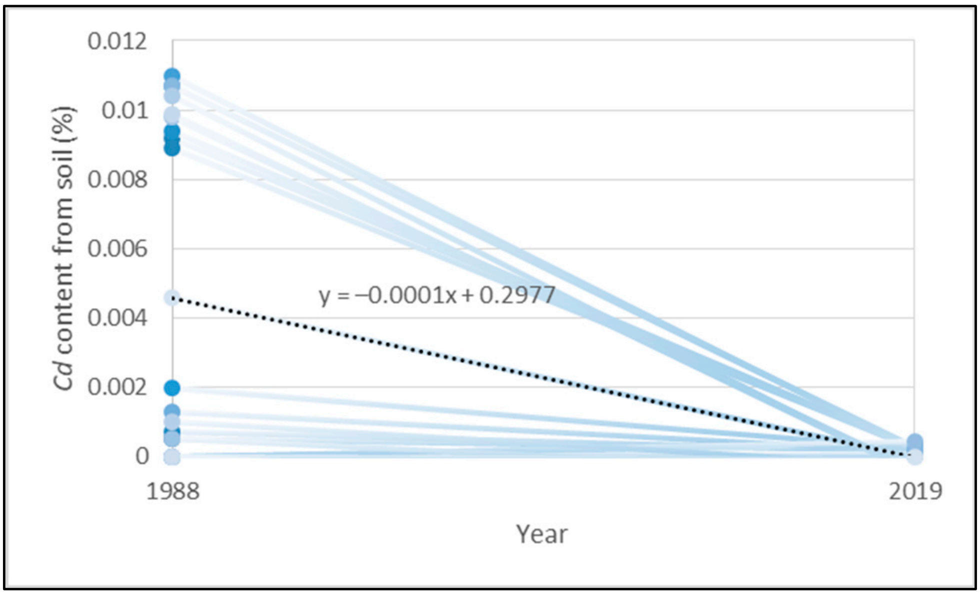


Figure 4. Decrease in Cd content (%) from Moldova Nouă's waste heap soil during 1988–2019 (Pattern no. 2; color lines express the correspondence between analysed samples in 1988 and 2019).

In all of the above cases, where significant differences exist between the variation of the concentration of chemical elements from the waste heaps' soil, the increase for Fe and decrease for Zn and Cd are given by linear monotone increasing and decreasing functions that have the following form:

$$y = 0.0852x - 163.97, \text{ for Fe;}$$

$$y = -0.0001x + 0.2842, \text{ for Cd.}$$

In the above models, y represents the chemical element's concentration and x represents the year. The above models were calibrated by using the averages of chemical elements' concentrations from 1988 and 2019 during their elaboration, the years between which significant statistical differences were obtained by using the ANOVA test.

The fitting of obtained models was tested by using χ^2 for goodness of fit between observed values for the concentration of chemical elements and expected values for chemical concentration obtained using the above models for Fe and Cd (Table 6).

Table 6. Data used for statistical testing models for goodness of fit.

Chemical Element	χ^2 Values	Confidence Level	Degree of Freedom	Critical Values of χ^2
Fe	8.091	95%	28	27.336
Cd	2.375	95%	28	27.336

As can be observed, χ^2 obtained by testing all elements is lower than the critical value of χ^2 for a specific degree of freedom. This means that the proposed models fit the experimental data and, with 95% confidence, the observed data follow the distribution from the proposed models.

3.3. The Influence of Forest Vegetation on the Soil's Chemical Composition Variation in Forest Plantations from Waste Heaps

As was shown previously, significant differences between the concentration of some micro, macro, and potentially toxic elements are present in most cases between V1 and V7 (determined in 1988) and V8 and V14 (determined in 2019). A part of these significant differences and some of the amplitudinal values of other elements from Table 2, determined in 2019, can be explained by the influence of forest vegetation planted on the waste heaps. By using the Shapiro–Wilk test and Kolmogorov–Smirnov test, we tested the normality of the tree number distribution in the sample surfaces, as well as the normality of the average distributions of biometric characteristics measured in the sample surfaces (563 trees in seven sample surfaces) (Table 7).

Table 7. Shapiro–Wilk and Kolmogorov–Smirnov tests for testing the normality of tree number distribution, their height, and diameters on plots.

Tested Variable	Mean	Standard Deviation	Shapiro–Wilk (S-W) Test		Kolmogorov–Smirnov (K-S) Test	
			S-W Test Value	*p*-Value	K-S Maximum Values	Critical Values (n = 7, alfa = 0.05)
Number of trees	80.429	17.194	0.900015	0.3756	0.18999	0.483
Height of trees (m)	5.057	0.976	0.7897	0.40721	0.19307	0.483
Diameter of trees (cm)	4.579	0.635	0.843857	0.126031	0.19077	0.483

As it can be seen, testing the normality of the variations' distribution with the Shapiro–Wilk test proved that the p-value > 0.05 in all cases (for the number of trees, height, and diameter). With a confidence level of 95%, we can retain the null hypothesis which states that the variables are normally distributed. The Kolmogorov–Smirnov test confirms this fact, with K-S maximum values having in all cases smaller values than the critical values of the K-S test (0.483 for n = 7 and α = 0.05). So, the null hypothesis is rejected, assuming that the sample data are normally distributed.

The influence of forest vegetation on the soil's chemical composition variation was studied regarding the chemical elements for which significant statistical differences were emphasized previously in regard to their content in soil (Fe, Zn, and Cd). This was obtained by correlating these differences with some stand characteristics in the sample surfaces, such as the number of trees from the sample surface, the trees' average height, and diameter, the tree volume, the stand consistency (expressed as percentage soil coverage by the crown), the oleaster percentage—this being the main species used in afforestation—and the black locust percentage, cumulated with the percentages of other species.

The average difference regarding Fe, Zn, and Cd concentration was calculated for plots where trees' biometric characteristics were measured (V8–V10), compared to analyses in that area before forest vegetation existed on the waste heaps (V1–V7 (Table 8)).

Table 8. The average differences regarding the Fe, Zn, and Cd concentrations (%) from V1 to V7 sampling points, compared individually with the V8–V14 sampling points.

Chemical Element	Sampling Points Where Biometric Characteristics Were Measured						
	V8	V9	V10	V11	V12	V13	V14
Fe	3.2669	2.8894	4.3791	1.4807	−0.1150	2.5655	4.2898
Zn	−0.0527	−0.0503	−0.0503	−0.0513	−0.0555	−0.0511	−0.0488
Cd	−0.0042	−0.0043	−0.0042	−0.0043	−0.0077	−0.0042	−0.0071

The averages of the statistically significant differences in concentration of each analyzed element (Fe, Zn, and Cd) were correlated with the stand's characteristics from sampling points V8 to V14 (Table 9).

Table 9. Stand characteristics from sampling points V8 to V14.

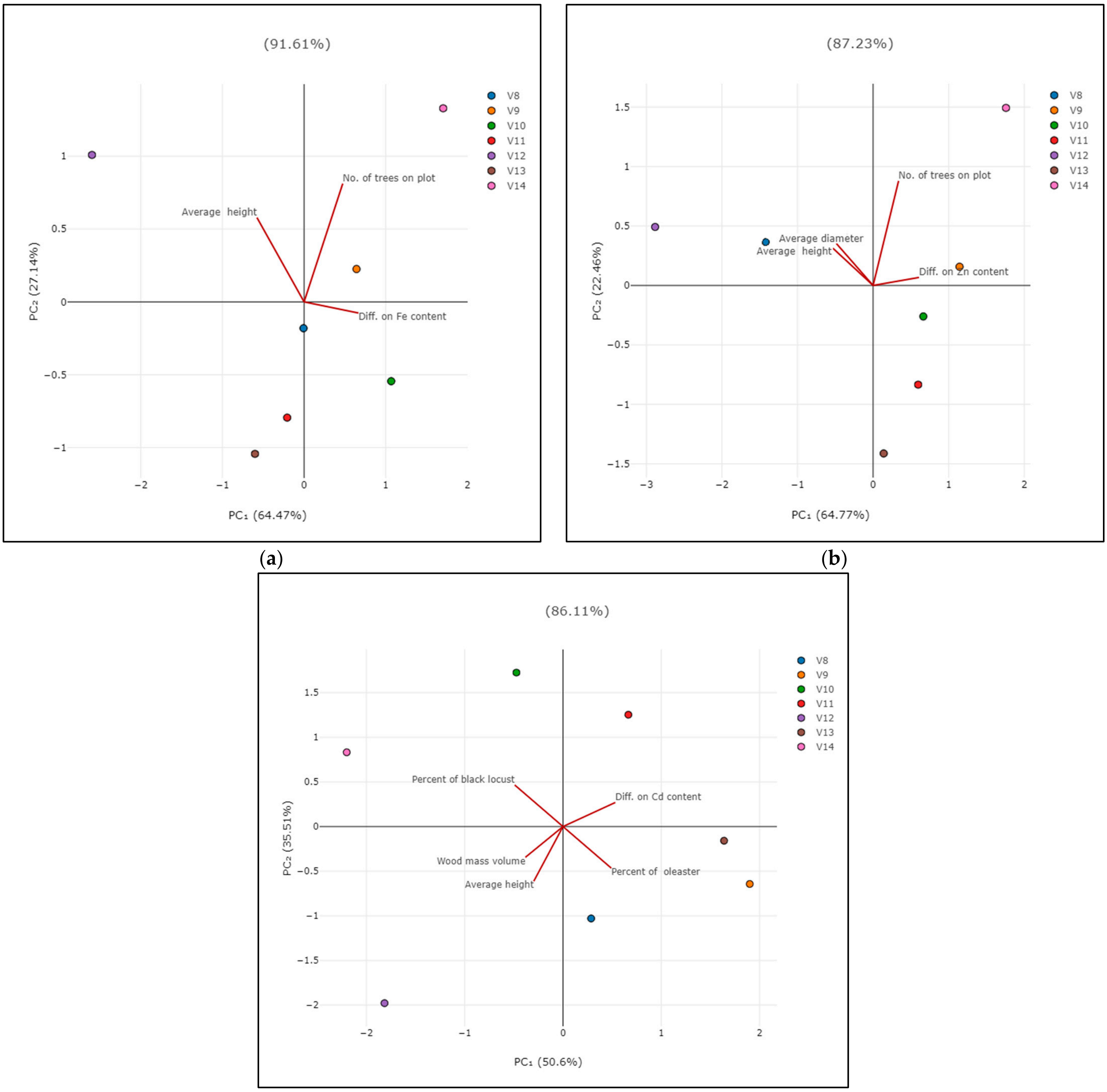
Sampling Points	No of Trees/Plot	Percent of Oleaster (%)	Percent of Black Locust and Other Species (%)	Average Height of the Trees (m)	Average Diameter of the Trees (cm)	Consistency—Percentage of Canopy Cover at Soil (1 to 10)	Wood Mass Volume (m^3)
V8	75	44	56	5.232	5.7067	9	1.1733
V9	91	53	47	4.6121	4.0824	10	0.6518
V10	79	22	78	4.3899	4.5633	9	0.6922
V11	73	33	67	4.211	4.244	9	0.5042
V12	73	36	64	7.1247	5.1863	9	0.9706
V13	59	47	53	4.9949	4.0237	8	0.4295
V14	113	19	81	4.8345	4.2478	10	0.9544

By calculating the Pearson correlation coefficient between the different characteristics presented in Table 9 and the Fe, Zn, or Cd differences in concentration (2019 and 1988), we obtained both positive and negative correlation coefficients (Table 10). This fact shows the existence of a direct correlation as well as a reversed correlation. They are presented below for each stand characteristic, together with the obtained correlation coefficients.

Table 10. Pearson correlation coefficients value (*r*) between Fe, Zn, and Cd differences in concentration (2019 and 1988) and different stand characteristics (*—reasonable correlation, **—high correlation, ***—very high correlation).

Pearson Correlation Coefficients Value (*r*) for Different Stand Characteristics and Differences on Chemical Element Content							
Chemical Element	Number of Trees	Average Height of Trees	Average Diameter of Trees	Consistency—Percentage of Canopy Cover at Soil	Wood Mass Volume	Percentage of Oleaster	Percentage of Black Locust and Other Species
Fe	0.5 *	−0.67 **	−0.2	0.29	0.07	−0.34	0.34
Zn	0.56 *	−0.84 ***	−0.68 **	0.38	−0.34	−0.29	0.29
Cd	−0.20	−0.72 **	−0.19	−0.31	−0.48 *	−0.42 *	−0.42 *

Based on the Table 10 data regarding the significance of correlation between differences in chemical element content, a Principal Component Analysis (PCA) was performed between each above element and variables for which a significant correlation exists (Figure 5).



(**c**)

Figure 5. The relationships between differences in chemical element content (2019 and 1988) and some stand characteristics of sample surfaces, as follows: (**a**) the relation between differences in Fe content and variables, as the figure indicates; (**b**) the relation between differences in Zn content and variables, as the figure indicates; (**c**) the relation between differences in Cd content and variables, as the figure indicates.

As can be seen, the highest correlation of chemical element differences in concentrations of Fe, Zn, and Cd from waste heap soils was determined for each stand's average height. The correlation between average height and the Zn content difference between

2019 and 1988 is reversed and very high ($r = -0.84$), while the one between average height and Fe and Cd content differences is reversed and high. Another high correlation was also identified between another biometric characteristic, namely average diameter and the Zn content difference from the waste heaps' soil between 2019 and 1988.

As for the other macro elements (P, K, and Mg), micro elements (Cu, Ni, and Mn), and potentially toxic elements (Cr) whose content in the waste heaps' soil was analyzed exclusively in 2019, significant correlations with some stand characteristics were identified only for P, Cu, and Mg (Table 11).

As can be seen, taking into account the negative correlation (except the no. of trees per plot), forest vegetation contributes to a decrease in Fe, Zn, and Cd in soil. In the case of a high density forest with a great canopy cover, the variation in the content of Fe and Zn is positively correlated with the number of trees per plot.

Table 11. Pearson correlation coefficients (r) between P, Cu, and Mg and different stand characteristics (*—reasonable correlation, **—high correlation, ***—very high correlation).

Chemical Element	Average Height of Trees	Average Diameter of Trees	Wood Mass Volume
P	0.87 **	0.81 ***	0.57 *
Cu	−0.66 **	−0.36	−0.06
Mg	−0.61 **	−0.38	−0.62 **

The PCA analysis showed an important influence of average tree height on P content (Figure 6). Between P content and average height, there is a very high correlation (Table 11).

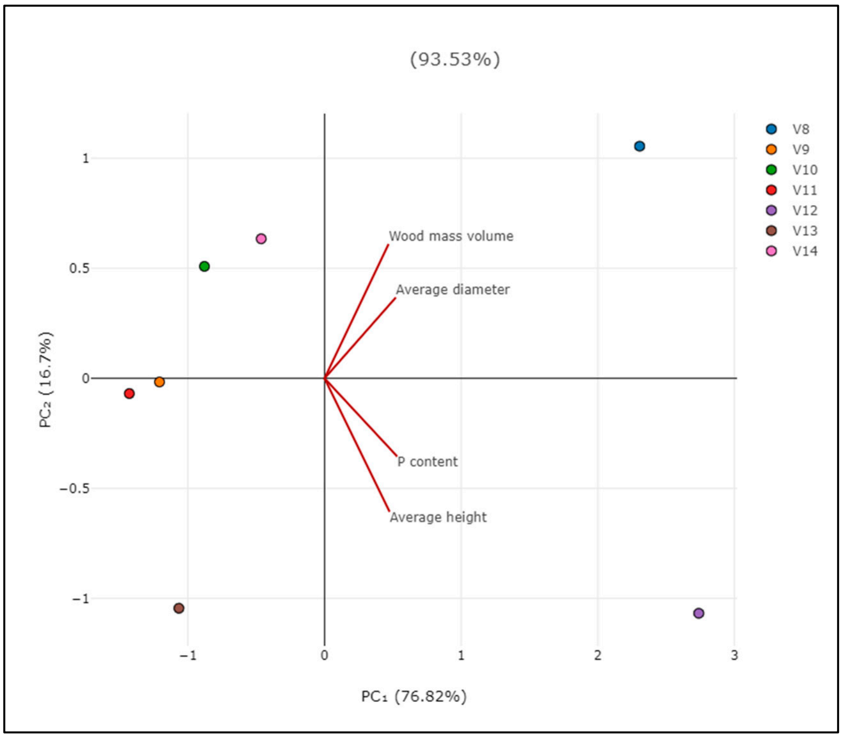


Figure 6. The relation between average height, average diameter, and wood mass volume in the sample surfaces and the P content.

Forest vegetation contributes to a reduction in Cu and Mg content in soil, with the correlation of stand characteristics being negatively correlated with the content of these elements in the soil. On the other hand, P content in soil is improved due to forest vegetation, with all correlations of stand characteristics of this element being strong and positive.

4. Discussion

4.1. The Chemical Composition of the Sterile as a Planting Substratum and of the Soil from Forest Plantations

Mining sterile can represent a serious threat to our environment [27]. Identifying and evaluating the risks of soil pollutants based on heavy metals has become a major preoccupation at a global level [28,29]. Some investigations have determined the base values of heavy metals in soils as well as multiple indices for the assessment of soil pollution, using the unique factor index (Pi), the geological accumulation index (Igeo), the Nemerow index (Pn), the ecological risk index (ER), and the health risk index (HI) [30]. Solving the issue of heavy metal pollution is one of the main preoccupations of society [31,32]. The toxicity, non-biodegradability, and mobility of heavy metals cause big damage to the agroenvironment [33,34]. The toxicity of heavy metals depends on their form of mobility according to their tendency for migration into substrates. Heavy metals in mixtures of sludge–soil—as in Moldova Noua waste heaps—showed lower mobility compared to soil matrices, but a similar level of concentration [35]. An important role in the mobility of heavy metals in soil is played by the pH of the soil. Increasing the pH induces a greater retention of metals in soil particles and conducts metal immobilization within soil [36]. With this considered, further reforestation work can take into account to use of species that, through the litter produced, lead to a decrease in soil pH.

Mining activities produce a large number of heavy metals and potentially toxic elements [37], such as copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), and chromium (Cr). They cause significant damage to the usage of nearby soil and vegetation growth [38]. In the soil from the Băiuț-Varatec mining area, near Baia Mare, Maramureș County, northwest Romania, the soil's contamination with heavy metals through the mine's acidic drainage had a large impact on the environment [39].

The species chosen to belong to the mining area's habitat should be well adapted to the local climate, as the soil is much degraded by the lack of organic matter and nutrients, as well as by a high concentration of heavy metals [40]. In the abandoned mining sites, the geoaccumulation index and the enriching factor for heavy metals indicate extremely high contamination. The waters near the mines have an acid pH, while the nearby agricultural fields present high values for heavy metals [41].

Tree and bush species have a great ability to tolerate and accumulate Cd, Cu, Pb, Zn, and As [42]. The diversity specific to stands can lead to a reduction in these types of heavy metals in the soil content. However, other investigations have indicated a limited transfer of heavy metals from soil to root. The heavy metal concentrations from the organs of fructiferous trees cultivated on the waste heaps were the heaviest in roots and leaves, with only zinc being situated within normal limits [43].

In some stibnite exploitations, the tailings are characterized by high SiO_2 concentrations, elevated MgO contents, moderate to low Al_2O_3, Fe_2O_3, and K_2O contents, and an especially striking lack of CaO [44]. In a similar manner, the present article has shown an initially high SiO_2 content (31.82% average value) and low Al_2O_3 in waste heaps from copper exploitation. Al_2O_3 was identified in a single experimental sampling point.

Sulfides are an important component, in total being 4.58%. The researchers determined that the total amount of sulfide sulfur in tailings is 21,000 tons, with an average content of 2.16%. The characteristic geochemical feature of tailings is a high concentration of toxic chemical elements: copper (4461.8 g/t), arsenic (2.421 g/t), and lead (1.758 g/t) [45]. SiO_2 (31.82%) and CaO (15%) are predominant in the sterile from Moldova Nouă copper waste heaps. Fe (5,33%) and S (1.48%) are present in average quantities, while heavy metals, rare ones, and Al_2O_3 are in low quantities (under 1%). All other compounds are weakly represented or appear only as traces. However, chemical analyses on the tailings from mines where Au, As, Bi, and Fe were extracted using other technologies revealed that soils were seriously contaminated with several heavy metals and As [46].

The analysis of the chemical composition of technogenic waters in the tailing dumps has shown that these waters contain a lot of trace elements with many of them exceeding the maximum permissible concentrations: total Fe (up to 1908 mg/L), Mn (up to 364.7 mg/L), Al (up to 54.3 mg/L), Zn (up to 71 mg/L), and Pb (up to 0.1). The content of total organic carbon is small (1.3–7.27 mg/L) while the concentrations of rare-earth elements are quite high [47]. Even though the quantities determined in water cannot be compared with the ones determined in the soil from the present article, we can see a similar ordering regarding the concentration of the above-mentioned elements. The controlling and successful prevention of wastewater from these areas containing cooper is important for the safety and health of plants, animals, and people and for the conservation of ecological environments [48]. Even if vegetation has a special capacity to reduce the amount of heavy metals in the soil, the wastewater from the preparation of ores can be treated using new technologies, such as the use of selective absorption materials. [49]

The average chemical composition of loparite tailing dump exploitation shows a weight percentage composition as follows: SiO_2—48.255; TiO_2—0.975; Al_2O_3—23.085; Fe_2O_3—5.105; FeO—0.59; MnO—0.215; CaO—1.48; MgO—0.43; K_2O—4.345; Na_2O—13.475; P_2O_5—0.665; SrO—0.285; and F—0.0745; SO_3—0.075 [50]. In the case of the waste heaps from Moldova Noua, the initial percentage concentrations of some elements are similar: SiO_2—31.82; Fe—5.33; S—1.48; Mn—0.059 (in the afforested waste heap); Mg—1.165 (in the afforested waste heap); and CaO—15; K—0.02396 (in the afforested waste heap). Carbonates have also been identified as a sink of metals [51].

4.2. Soil's Chemical Composition in Forest Plantations from Waste Heaps and the Influence of Forest Vegetation on These Variations

The variation of the chemical composition for some elements from the waste heap's technosoil is highly and very highly reversely correlated with the stand's dimensional characteristics such as height ($r = -0.67$ for Fe; $r = -0.84$ for Zn; and $r = -0.72$ for Cd), diameter ($r = -0.68$ for Zn), and volume ($r = -0.62$ for Mg). As such, the stand's structural diversity and characteristics play an important role in improving the content of heavy metals in the soil. These characteristics are especially dependent on age, an aspect that was emphasized by other investigations regarding the fertility of technosoils. Such studies show that stand-age-dependent forest attributes have a significant positive relationship with total exchangeable bases, litter stock, and community composition, being the best predictors for explaining an increase in fertility for technosoil [52].

The bioaccumulation factor of Cu has a positive correlation with the most mobile fractions of Cu in soils, and once absorbed is immediately translocated to leaves [53]. This high Cu bioaccumulation capacity can lead to a high reversed correlation between Cu soil content and tree height, as we obtained ($r = -0.66$). The contact of tree roots with tailings, in afforested areas with topsoil, resulted in high concentrations of Cu in the roots, even if the roots did not penetrate the tailings layer after two growing seasons [54]. In the case of the present study, the roots are deeply in the tailing, taking into account tree height and age. The height of the trees does not necessarily have a high correlation with the biomass of the roots [55], but strongly influences the crown's size and, implicitly, the capacity of translocating mobile Cu fractions to leaves [53]. The same thing happens for Cd which is very mobile in plants, being easily adsorbed by roots, transferred, and accumulated in leaves and the stem [56], showing a positive correlation between the stem and leaf [55]. In the case of the present paper, the Cd content variation from the waste heap's soil is highly correlated with the stand's average height ($r = -0.72$).

On the fields of afforested waste heaps, the minimum Zn and Pb concentration overlaps with a sudden Cu concentration decrease, due to afforestation [57]. This fact is also confirmed by the present article, which shows that the difference in the soil's zinc content decreases as the diameter increases, especially for height, similar to Cu. Regarding taxa used in afforestation on waste heaps from Moldova Nouă, the species used have the important contribution of removing heavy metals from soil. It is demonstrated that, on forest plantations on waste dumps, more than 92% of Cu and more than 46% of Pb were removed by black locust [15], even eith Pb being one of the heavy metal pollutants which is difficult to biodegrade [58]. The persistence of Cu in the soil over time is also due to the Cu-O bonds, which are very stable due to the charge distribution around the Cu atoms [59]. In addition to the fact that it is persistent in the soil, copper is itself a rich trace element, having a widespread status and being found in rocks and minerals [60].

Regarding sea buckthorn—another species used in afforestation on waste heaps from Moldova Nouă—it was observed that, after 10–20 years from a plantation, degradation processes were stopped and the soil was ameliorated [61]. Other similar research has shown that the soil samples collected from waste dumps that were not forested are much richer in toxic elements such as Pb, Cu, Cd, Zn, Bi, and As [10]. Research that studied heavy metal concentrations according to depth level showed that concentrations did not vary significantly except for Pb and Zn. For both, the concentration was higher in the first layer of 0–15 cm, followed by the level of 15–50 cm and by a deeper layer of 50–100 cm, respectively [62].

High total Fe concentrations were reported in natural soils by similar studies [53], a similar situation with the waste heaps from Moldova Nouă, where the Fe concentration was higher in 2019 (7.97%) compared with 1988 (5.33%). The Fe bioavailable concentrations were low and this indicates a positive correlation between Fe and their concentrations in the residual fraction [53].

Other research showed that organic amendments, such as aged cattle manure, significantly increased heavy metal concentrations in the leachate, and decreased heavy metal concentrations in soil [63]. Leaching tests showed that large amounts of heavy metals can be released from waste dumps by precipitations [64]. Similarly, in our case study, the organic layer from the litter above the soil, resulting from leaf decomposition, contributed to the decreasing of heavy metal concentrations in the soil. This can contribute also to the oxidation of sulfide minerals combining heavy metals, and can contribute also to the dissolution of heavy metals by rainwater [65].

5. Conclusions

Analyses regarding the current chemical composition of soils from waste heaps indicate a decrease in potentially toxic elements such as Cd and Pb during a 30 year period, as well as a concentration of some micro elements such as Fe, and some macro elements, such as Ca. These were recorded on the background of a decrease in heavy metal percentages, as well as other soil compounds that were levigated or absorbed at a radicular level. As we shown above, the decrease in heavy metal concentrations is due to the forest species used, contributing to the removal of heavy metals from soil, a fact demonstrated and sustained also by other studies [15]. The leaching process influenced by wood plants through the radicular system and litter from above the soil can contribute to the reduction of heavy metal content from waste soil.

Significant differences regarding the Fe, Zn, and Cd concentration variations from the waste heaps' soil were identified. At the same time, we created models regarding the variation in time for the content of Fe and Cd. The created models contribute to the understanding and estimation of the changes over time in the concentration of these heavy metals in the soil of similar waste dumps or can be used as a basis for the creation of more complex similar models.

Variations in time for Fe, Zn, and Cd and the actual content of P, Cu, and Mg are correlated especially with the average height of trees (positive for P and negative for others), as well as with the average diameter (for Zn and P), wood mass volume (for Cd, P, and Mg), the number of trees (for Fe and Zn), and with percent of oleaster and black locust (for Cd).

Further research directions can be conducted to investigate the contamination status of heavy metals in groundwater, of the running waters in the immediate vicinity (Danube), and of nearby soil.

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writing—original draft preparation, I.-C.C. and D.S.P.; writing—review and editing, E.A., A.B. and V.E.C.; visualization, I.-C.C., D.S.P., E.A., V.E.C., A.B., N.C., S.R., T.-M.G. and O.B.; supervision, E.A. and V.E.C.; funding acquisition, S.R. and N.C. All authors have read and agreed to the published version of the manuscript.

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