Article

The Distribution of Metallic Elements among Humus Substances in Soil from Volcanic Rocks

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Abstract: The ability of humus substances to form stable complexes with inorganic and organic soil constituents plays a vital role in the generation of environmental pollution, migration, and pollutants transformation. This paper deals with the study of the sorption of metallic elements (Al, Ca, Cu, Fe, K, Mn, Mg, Zn) in Andosols, Cambisols, and Planosols on Slovak soil types based on the detection of the quality and quantity of humus substances and soil textural properties. Five soil profiles from two areas in the central part of the Western Carpathians on volcanic rocks in Slovakia were investigated. HS values increased with Al, Ca, Cu, Fe, K, and Mg. Fe, Al, Ca, Mg, K, Mn, Cu, and Zn increased with the FA fraction. Al, Ca, Fe, K, and Mg were increasing with increasing HA values. In the HA fraction, a very tight relationship was among K and Fe contents (r = 0.902). In the FA fraction, we found with increasing Cu content, Ca content also increased (r = 0.959). The HS values were positively correlated with the silt and negatively correlated with the clay and the sand fraction. Only the elements Mn and Zn in Planosol were below the detection limit. High concentrations of metallic elements were in Andosol.

Keywords: Kremnica Mountains; humic acid; fulvic acid; cations; grasslands

1. Introduction

Humus substances (HSs) are the most widespread organic substances group in the natural environment and have high stability [1]. The ability of HSs to form stable complexes with soil's inorganic and organic components plays a crucial role in developing environmental pollution and the migration and transformation of pollutants [2,3]. The protective function of an HS can link different types of contaminants [4]. HSs can also act as a "geochemical barrier" [5]. HSs contain functional groups capable of interacting with metal ions to form complexes [6]. The main functional groups of HSs capable of binding metal ions are carboxyl, amino, and hydroxyl groups. According to Burlakovs et al., humus substances have a good ability to diminish the content of biologically available heavy metals and form complexes with metal ions depending on the soil and metal type and concentrations of HS in the soil [1]. Therefore, HSs can improve many soil properties, e.g., plant productivity and nutrient uptake [2].

Soil pollution by heavy metals affects the quality of the whole environment and leads to serious environmental consequences. Risk elements can also be transported, e.g., by wind or water (precipitation) [7–10], and deposited on the soil, thereby contaminating it [11–13]. Heavy metal pollution affects not only crop yields and crop quality, but also the atmosphere and the aquatic environment. Food chains also affect human health. Humussoil or humussoil with hydroxyapatite are appropriate amendment materials for decreasing the mobility of heavy metals [14,15]. Heavy metals may be bound or sorbed by particular natural substances, increasing or decreasing mobility [16], e.g., montmorillonite, illite, kaolinite, hydrous oxides of Fe and Al, humic acids, and fulvic acids. Soil organic amendments such as manure, compost, peat, biochar, clay minerals, phosphate compounds, coal fly ash, and liming materials are widely used as immobilising agents for potentially

toxic elements (PTEs) [17,18]. They contain a high proportion of humified organic matter (OM), which can decrease the bioavailability of heavy metals in soil by adsorption and forming stable complexes of humus substances [17,19,20].

HSs can significantly reduce the acute toxicity and bioavailability of metals [21]. These amendments can reduce the bioavailability of potentially toxic elements (PTE) in soils through diverse mechanisms such as precipitation, complexation, redox reactions, ion exchange, and electrostatic interaction [18]. There are two types of metal ion binding mechanisms of HSs: covalent binding, where each attached atom donates one of the associated electrons, and coordinate binding, where a metal atom accepts a pair of non-metal electrons. This binding process among HS and metal ions is usually fast. Humic-metal complex stability may differ for different metals. Humic acids (HAs) and fulvic acids (FAs) are part of HSs and are ubiquitous in the natural environment, effectively influencing the removal and transportation of heavy metals [22]. The strong complex abilities of metal ions and HA/FA could also influence the underlying mechanisms involved in the interaction among the three components (heavy metals, HA/FA, and soil). For example, metals such as Hg, Cd, and Pb have higher stability, while Ca, Na, Mg, and Zn are lower [23].

Humic acids are present in high concentrations in stabilised organic materials. Humic acids contain many carboxylic and phenolic OH groups that generate Brønsted acidity [24–26]. Most of these groups are reactive under acidic conditions. The humic acid surface has an overall negative charge even at a low pH range (pH = 3–5) [27]. HAs are complex natural acidic-organic macro-molecules with highly variable chemical compositions and diverse, active functional groups [28]. These HAs can affect mobility and heavy metals' bioavailability when these materials are used as organic amendments in soils [19]. Organic macromolecules play an essential role in the transport, bioavailability, and solubility of heavy metals [29].

Globally, permanent grasslands (PGR) are a significant terrestrial ecosystem covering 26% of the world's land area and 28% of the total agricultural area [30]. PGRs provide various ecosystem services (e.g., forage production and mitigation of global warming through carbon storage) [31–34]. However, these services can be threatened by pollutants containing elements at risk [35]. The circulation and migration of metals in the natural environment are mainly related to rock decay, volcano eruptions, and soil formation processes [36–39]. Metal mobilisation depends on soil characteristics and is controlled by the soil matrix and composition [40–42]. The addition of the humus substances immobilises some heavy metals [43] and profoundly affects the behaviour of metals in the environment [44]. In general, humic acids (HAs)/fulvic acids (FAs) and heavy metals exist simultaneously in the environment, where they may affect each other's behaviour [45–48].

The Kremnica Mountains represent a type of mountain landscape with a subtype of the polyfunctional mountain landscape. Mining activities and the establishment of dispersed settlements have contributed to the reduction of forest cover and the expansion of pastures. As the Kremnica Mountains are also a volcanic mountain range, the metallic elements Al, Ca, Cu, Fe, K, Mg, Mn, and Zn were chosen for the analyses.

The aim of this paper is to show the distribution of eight metallic elements (Al, Ca, Cu, Fe, K, Mg, Mn, Zn) relating to the amount of humic and fulvic acids in three soil types of *Andosol*, *Cambisol* and *Planosol*. Furthermore, the distribution of metallic elements concerning humus substances and soil textural characteristics of selected Western Carpathian (Slovakia) areas was analysed.

2. Materials and Methods

2.1. Study Area

The measurements were carried out at two different sites (*Localities I–II*) in the central part of the Western Carpathians (in the Banská Bystrica region, in the Žiar nad Hronom district) on volcanic rocks in Slovakia to different depths (see Figure 1). Selected localities and soil sampling locations were classified into geomorphological units in Slovakia based on regional geomorphological zonation [49]. In addition, soil sampling was carried out in a meadow (mown meadow, xerothermic meadow, pasture) in the Kremnica Mountains.
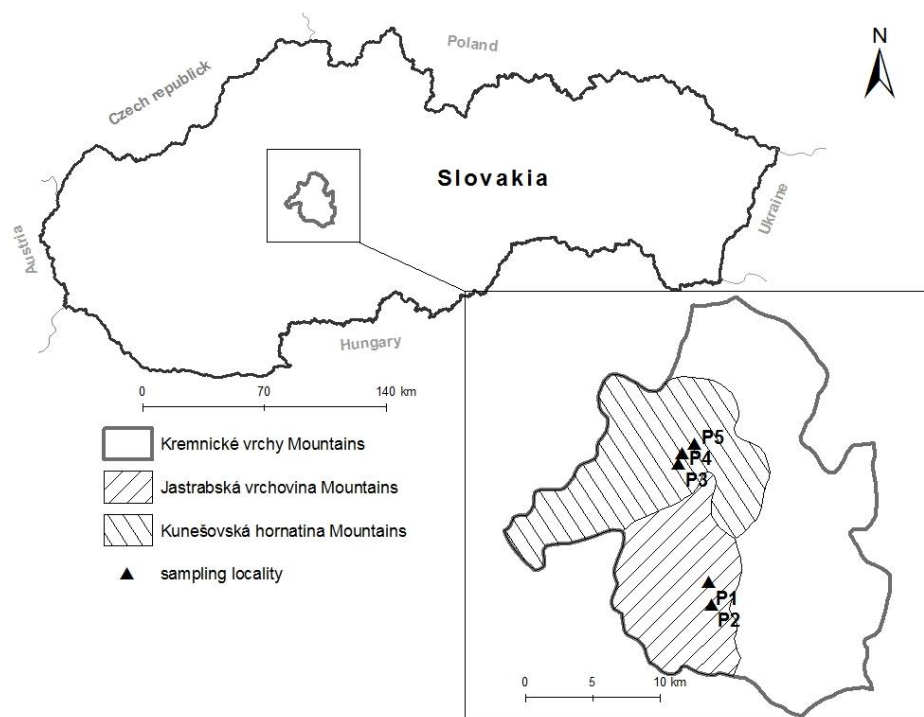
Figure 1. Jastrabská vrchovina Mts. and Kunešovská hornatina Mts.: localities of soil samples (*P1–P5*).

The Kremnica Mountains are a volcanic mountain range, and their geological structure is based on lava bodies. Andesites and their tuffs build the bulk of the mountain range in a continuous unit, and rhyolites and their tuffs are mainly concentrated in the southwestern part of the mountain range adjacent to the Žiar basin [50]. The Kremnica Mountains are located in the central part of Slovakia as part of the West Carpathians Province, the Inner West Carpathians Subprovince and the Slovak Central Mountains area. It borders the following geomorphological units: in the north are the Great Fatra and Turčianska Basin; in the west, Žiar, Hornonitrianska Basin, and Vtáčnik; in the south, the Žiar Basin and the Štiavnické Mountains; in a short south-eastern section, the Plišovská basin and Javorie; and in the east, the Zvolen Basin and the Staré Hory Mountains [49]. The Kremnica Mountains are divided into five geomorphological sub-units [50]:

1. Kunešovská hornatina Mts. in the northwestern part;
2. Jastrabská vrchovina Mts. in the southwestern part;
3. Flochovský chrbát Mts. in the central part and the north;
4. Turovské predhorie Mts. in the south;
5. Malachovské predhorie Mts. in the east.

Kremnické Bane belongs to the foothill stage (500–800 m above sea level) and the mountain stage (800–1500 m above sea level) based on the vertical division. Jastrabá belongs to the hilly stage (200–500 m above sea level), and Ihráč to the hilly stage (200–500 m above sea level and 500–800 m below mountain level). Andosols, Cambisols, Fluvisols (alluvial meadow soil), Pseudosols, and Ranker occur in the study areas.

Five soil profiles from two localities, Jastrabská vrchovina Mts. (*P1–P2*) and Kunešovská hornatina Mts. (*P3–P5*), were studied (see Figure 1). The studied soils were *Andosols, Cambisols and Planosols* (see Table 1). According to standard procedures, samples were collected from each genetic horizon, and the diagnostics were made by the World References Base taxonomy [51]. Characteristics of soil horizons are presented in Table 2 [52].

Table 1. Characteristics of soil samples localities.

Localities/Cadastre Territory	Profiles	Coordinates	Altitude [m. a. s. l.] [2]	Position	Type of Land	Slope Relief	Soil Unit De Signation According to BPEJ [1]
Locality I/Jastrabská vrchovina Mts.	P1	48°38′35.4″ N 18°55′46.3″ E	486	slope	mowed meadow	12–17°	Eutric Cambisols (EC)
	P2	48°37′41.8″ N 18°56′00.2″ E	430	slope	mowed meadow	17–25°	Eutric Cambisols (EC)
Locality II/Kunešovská hornatina Mts.	P3	48°43′13.7″ N 18°53′23.0″ E	944	saddle	xerothermic meadow	12–17°	Eutric Andosols (EA)
	P4	48°43′38.0″ N 18°53′34.0″ E	872	slope	mowed meadow	7–12°	Eutric Cambisols (EC)
	P5	48°43′59.7″ N 18°53′22.0″ E	808	slope	mowed meadow	3–7°	Eutric Planosols (EP)

[1] Soil unit designation according to BPEJ (BPEJ is the soil evaluation method on the territory and nationally used table for classifying how land is used) [53]. [2] m. a. s. l. = metres above sea level.

Table 2. Morphological description and identification of soil horizons.

Profile	Soil Types	Identification	Depth [m]	Characteristics
P1	Eutric Cambisol	Ao	0.0–0.12	light brown ochric A-horizon, damp, loose, micro-lumpy structure, without coating and neologism, colour by dry 10YR 4/2
		Bv	0.12–0.35	brown to reddish-brown sub-horizon of cambic B-horizon formed by sand, damp, loose, grained-polyhedral structure, without coating and neologism, colour by dry 10YR 4/3
		C	>0.35	diluvium of sandy substrates, damp, cohesive, loamy, colour by dry 10YR 6/3
P2	Eutric Cambisol	Ao	0.0–0.07	light brown ochric A-horizon, damp, loose, micro-lumpy structure, without coating and neologism, colour by dry 10YR 5/2
		Bv	0.07–0.36	brown to reddish-brown sub-horizon of cambic B-horizon formed by sand, moist, loamy, polyhedral structure, without coating and neologism, colour by dry
		C	>0.36	loamy-clayey diluvium, damp, cohesive, loamy, colour by dry 10YR 7/1
P3	Eutric Andosol	Ol	0.0–0.06	the overlying organogenic and terrestrial horizon with plant remains, loose, dry, colour by dry 10YR 3/4
		Aau	0.06–0.09	brownish-black, extremely fluffy and humic andic A-horizon, damp, loose, micro-lumpy structure, without coating and neologism, colour by dry 10YR 3/3
		Bva	>0.09	dark brown, mellow, strongly humic cambic-andic B-horizon, damp, cohesive, loamy, small and medium stones, colour by dry 10YR 4/3
P4	Eutric Cambisol	Ao	0.0–0.06	greyish-brown ochric A-horizon, damp, loose, micro-lumpy structure, without coating and neologism, colour by dry 10YR 4/3
		A/Bv	0.06–0.20	brown to reddish-brown transition, with hints of hydromorphic, moist, loamy, polyhedral structure, without coating and neologism, colour by dry 10YR 4/6
		Bv	0.20–0.50	clayey-loamy, brown to reddish-brown sub-horizon of cambic B-horizon, colour by dry 10YR 5/6
		C	>0.50	loamy diluvium, damp, cohesive, loamy, colour by dry 10YR 6/7
P5	Eutric Planosol	Ao	0.0–0.15	light to greyish-brown ochric, sorption unsaturated A-horizon, damp, loose, micro-lumpy structure, without coating and neologism, colour by dry 10 YR 5/3
		A/En	0.15–0.30	transitional horizon, with hints of hydromorphic, moist, loamy, polyhedral structure, without coating and neologism, colour by dry 10 YR 5/4
		En	0.30–0.60	light grey eluvial pseudo-E-horizon, developed by moving surface water and its effects on the soil organic matter, wet, loamy, featureless structure, a reddish-brown coating on the sand grains, colour by dry 10YR 5/5
		Bmv	>0.60	speckled marble pseudo-B-horizon (representation of grey and rusty colour in the matrix above 80%), cohesive clay-loam diluvium with signs of gleyic properties, loamy sand with an admixture of gravel (up to 10%), colour by dry 10YR 6/6

EC (Ao, Bv, C)—soil profile *P1* of *Eutric Cambisol*, EC (Ao, Bv, C)—soil profile *P2* of *Eutric Cambisol*, EA (O1, Aau, Bva)—soil profile *P3* of *Eutric Andosol*, EC (Ao, A/Bv, Bv, C)—soil profile *P4* of *Eutric Cambisol*, EP (Ao, Ao/En, En, Bmv)—soil profile *P5* of *Eutric Planosol*.

We focused on localities within one district (Žiar nad Hronom) to show the differences in metallic element content and monitored parameters of meadow soil.

The monitored soil samples from the localities of Kunešovská hornatina Mts. and Jastrabská vrchovina Mts. belong to the warm climatic region. The altitude of the soil sampling localities in the Jastrabská vrchovina Mts. ranges from 430 m a.s.l. to 696 m a.s.l. In the Kunešovská vrchovina Mts., the monitored soil sampling from localities range from 808 m a.s.l. to 944 m a.s.l. According to Špánik et al., annual precipitation depends on increasing altitude [54].

2.2. Equipment and Analytical Procedure

The analysis included a series of measurements such as TOC, HS, HA, FA, QHS, NT, soil texture, pH, and metal element analysis using atomic absorption spectrometry on soil samples collected from autumn 2019 to spring 2020. During this period, 180 soil samples were taken from 2 selected localities (3 soil types) and used as meadows (*Localities I–II*). Soil samples were taken from different depths (from 0.0 m to >0.60 m) (see Table 2). The analyses of all soil samples, e.g., pH and TOC, were repeated three times, and further ana-lyses, e.g., N_T, silt, sand and clay fractions, were repeated twice. The data presented in the tables are the arithmetic mean values.

The result was the total content of metallic elements (Al, Ca, Cu, Fe, K, Mg, Mn, and Zn) from the analysed soil samples. In addition, the contents of metallic elements were compared at different depths, soil types, and under different land uses.

Soil samples were collected with an Edelman soil auger and in the form of open soil probes from each soil horizon to avoid mixing two different soil horizons [55]. According to the Decree of the Ministry of Labour, Social Affairs and Family of the Slovak Republic No. 59/2013 Coll. and subsequent amendments for contamination detection, at least one average sample was taken from every area of 10 ha (at least nine sampling points/places) with homogeneous soil in the area under examination [56]. In addition, average samples were taken from each part for heterogeneous soil in the area mentioned.

2.2.1. Determination of Agrochemical Indicators, Contents of Nutrients, and Metallic Elements

For the analytical determination of metallic elements, limit values were used in air-dried soil samples. Soil samples as fine earth I (average 2 mm particle size) were used for measurements that determine metallic elements using the atomic absorption spectrometry method, and fine earth II (average 0.125 mm particle size) was prepared to determine agrochemical characteristics and nutrient contents.

Total Organic Carbon

According to the Tyurin method modified by Nikitina, we determined the total organic carbon content (TOC) in soil samples and the various separated fractions [57] (1).

$$\text{TOC} = \left(\frac{(a - b) * 0.003 * f * 1.17}{n} \right) * 100\%, \tag{1}$$

where $\underline{a}$ = consumption of 0.1 mol.dm^{-3} of a Mohr's salt solution for titration of the blank (cm^3), b = consumption of 0.1 mol.dm^{-3} of a Mohr's salt solution for titration of the sample (cm^3), 0.0003 = the conversion factor to carbon, f = the Mohr's salt titration factor, n = the soil mass (g), and 1.17 = the conversion factor for the complete reaction without the use of a catalysator (Ag_2SO_4).

Humus Substances

Humus substances were extracted into the $Na_4P_2O_7$ (c = 0.1 mol dm^{-3}) solution and adjusted to pH = 13 with NaOH (c = 1.0 mol dm^{-3}). The samples were left for infusion for 24 h. UV/VIS spectra were measured using a spectrophotometer (Specord 50 Plus, Analytik Jena, Jena, Germany) in a range from 300 nm to 700 nm.

The humus substances' (HSs') content was determined by the group composition of humus substances using the Belčiková-Kononová method [58]. The samples were extracted with the pyrophosphate solution (c = 0.1 mol dm^{-3}) over 24 h at room temperature (22 °C) with occasional shaking to determine the concentration of metals bound with humic and fulvic fractions. Undissolved material was removed by centrifugation at 3000 rpm [58]. The solution was acidified with H_2SO_4 and filtered to separate fulvic acids (FA) from humic acids (HA). The residue containing HA was dissolved with a hot 0.05 mol dm^{-3} NaOH. All solutions were filtered and adjusted to pH = 6 with 0.1 mol dm^{-3} H_2SO_4 and NaOH.

In all experiments, the chemical reagents (ACS grade) were dissolved using distilled and deionised (DDI) water produced using a MilliporeSigma™ Synergy™ Ultrapure Water Purification System (Meck Millipore, Bedford, MA, USA).

Colour Quotient and Humification Degree

The colour quotient of humus substances (QHS) was chosen as the absorbance values ratio at 465 nm and 665 nm from VIS spectra [59]. VIS spectrometry (Specord 50 Plus, Analytik Jena, Germany, glass cuvette) was used to determine the colour quotient.

From equation (2), we calculated the humification degree of humified substances [60].

$$H = \left(\frac{cHA}{TOC} \right) * 100\% \tag{2}$$

where TOC = total organic carbon, cHA = carbon of humic acids.

Total Nitrogen

The Kjeldahl method determined the total nitrogen (N_T) [61].

Soil Texture

Silt, sand, and clay fractions were determined according to the pipette method [62].

Soil Reaction

According to the van Reeuwijk method pH values in soil samples were analysed (water to soil = 2.5:1, *v:m*) [62]. The active soil reaction (pH(H_2O)) was determined in distilled water and the exchange soil reaction (pH(KCl)) in a solution of 1 mol dm^{-3} KCl (Centralchem, Ltd.; Bratislava, Slovakia). The solution was mixed. The suspension was shaken in a Unimax 2010 horizontal shaker (Heidolph Instrument, GmbH, Schwabach, Germany) for 20 min. After shaking, the samples were filtered through Filtrak 390 filter paper (Munktell & Filtrak, GmbH, Bärenstein, Germany). The pH values in the bath were measured using the pH meter ino-Lab Multi 9310 (Labo SK, Ltd., Bratislava, Slovakia) equipped with a plastic electrode with a temperature sensor.

Analysis of Metallic Elements

For the determination of the content of major elements (Al, Ca, Fe, K, Mg, Mn) and heavy metals (Cu, Zn), we used atomic absorption spectroscopy on the equipment GT AAS; Agilent Technologies, GTA 120 Graphite Tube Atomizer (Hermes LabSystems, Ltd.; Bratislava, Slovakia). Soil samples were measured in three replicates in a graphite atomic absorption spectrophotometer for all analysed elements' quantification. Before analysis, the soil samples were mineralised in Ethos One (Chromspec Slovakia, Ltd., Šaľa, Slovakia). Soil samples were mineralised in aqua regia (HCl = 37%; HNO_3 p.a. $\geq$ 65%; chemicals from Sigma Aldrich, Ltd.; Bratislava, Slovakia) to determine the content of major and heavy metals. Then, we analysed the results following the Decree of the Ministry of Agriculture and Rural Development of the Slovak Republic No. 508/2004 Coll. and with an amendment of certain acts [56].

2.3. Data Analyses

As previously mentioned, the measured values obtained from soil samples were analysed using selected statistical methods. The Spearman's rank correlation coefficient was applied to calculate the degree of interdependence among the observed variables [63]. The Spearman correlation was used to determine the relationship among the chemical properties, textural fraction, and content of metallic elements in soil samples. We performed the calculations in the STATISTICA program 9.0 Standard Plus CZ (StatSoft Inc., Tulsa, OK, USA).

3. Results

Soil samples were collected at *Localities I to II* in two seasons (autumn and spring). As mentioned above, pH(H_2O), pH(KCl), TOC, cHS, cHA, and cFA were monitored in the soil samples (see Table 3). *Andosols* had the lowest values of soil reaction. In *Andosols*, higher fulvic acid content was detected than humic acids (see Table 3).

Table 3. Mean values of pH, TOC, and carbon of fulvic and humic acids.

Soil Type		Andosol			Cambisols			Planosol		
	Unit	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
pHH$_2$O		5.280	6.070	5.700	5.630	6.500	5.912	6.080	6.320	6.190
pHKCl		3.860	4.610	4.208	3.750	4.970	4.560	3.980	4.760	4.275
TOC	%	2.867	13.050	7.432	0.142	4.838	1.530	1.354	5.271	2.653
cHS	%	1.000	9.196	4.212	0.216	1.887	0.654	0.731	1.799	1.188
cHA	%	0.149	1.474	0.823	0.009	0.404	0.147	0.114	0.439	0.226
cFA	%	0.509	9.047	3.389	0.035	1.483	0.507	0.617	1.360	0.962

(Characteristics label spans the rows above)

pH(H_2O)—active soil reaction, pH(KCl)—exchange soil reaction, TOC—total organic carbon, cHS—carbon of humus substances, cHA—carbon of humic acids, cFA—carbon of fulvic acids.

The highest amounts of organic matter in natural ecosystems, mainly from vegetation, accumulate in the uppermost parts of the soil profile. We compared the dependence of individual correlation values on sampling depth and pH (H_2O, KCl) values, in particular monitoring localities and soil types (see Table 4). In the context of increasing depth, the overall nature of the transformation processes was changing. Oxidation processes that result in carbon loss from the soil change to fermentation processes. As soil depth increases, the content of TOC, nitrogen, and another organic matter decreased.

Table 4. The values of carbon and nitrogen parameters in soil profiles.

Profile	Depth	TOC	HS	HA	FA	N_T	C/N	c(HA)/c(FA)	Q$_{HA}$	Q$_{HS}$	DH
	[m]	[%]	[%]	[%]	[%]	[mg kg^{-1}]					[%]
P1	0.00–0.12	3.14	0.93	0.26	0.68	5775	5.4	0.60	3.35	2.71	10.99
	0.12–0.35	0.91	0.26	0.04	0.23	1618	5.6	0.16	2.08	2.31	3.59
	>0.35	0.13	0.14	0.01	0.13	218	6.0	0.04	2.16	1.78	4.17
P2	0.00–0.07	5.37	1.85	0.37	1.48	10,150	5.3	0.25	4.49	3.21	6.84
	0.07–0.36	0.66	0.63	0.10	0.52	525	12.6	0.20	2.62	2.81	16.00
	>0.36	0.88	0.26	0.14	0.12	700	12.6	1.18	2.16	1.88	16.15
P3	0.00–0.06	14.77	6.84	1.22	5.63	28,350	5.2	0.22	5.97	6.28	8.24
	0.06–0.09	12.41	6.37	0.46	5.91	21,350	5.8	0.08	5.58	7.11	3.72
	>0.09	4.28	2.40	0.27	2.13	8225	5.2	0.12	3.83	4.68	5.83
P4	0.00–0.06	5.01	1.85	0.38	1.47	8400	6.0	0.26	4.29	3.44	7.53
	0.06–0.20	1.58	0.86	0.21	0.65	3850	4.1	0.32	3.84	2.59	13.27
	0.20–0.50	1.63	0.48	0.17	0.31	3850	4.2	0.53	2.95	2.54	10.29
	>0.50	1.35	0.59	0.13	0.46	2275	5.9	0.27	2.99	2.28	9.32

Table 4. *Cont.*

Profile	Depth	TOC	HS	HA	FA	N_T	C/N	c(HA)/c(FA)	Q_{HA}	Q_{HS}	DH
	[m]	[%]	[%]	[%]	[%]	[mg kg^{-1}]					[%]
P5	0.00–0.15	2.85	1.64	0.61	1.03	5075	5.6	0.59	4.20	3.67	21.37
	0.15–0.30	2.81	0.92	0.38	0.55	5425	5.2	0.69	3.92	3.33	13.45
	0.30–0.60	1.25	0.92	0.18	0.74	2275	5.5	0.24	3.47	2.65	14.24
	>0.60	1.10	0.67	0.21	0.46	1750	6.3	0.45	2.76	2.77	19.02

TOC—total organic carbon, HS—humus substances, HA—humic acids, FA—fulvic acids, N_T—total nitrogen, Q_{HS}—the colour quotient of humus substances, Q_{HA}—the colour quotient of humic acids, DH—humification degree.

The studied correlations among TOC and humic fractions are shown in Figure 2.
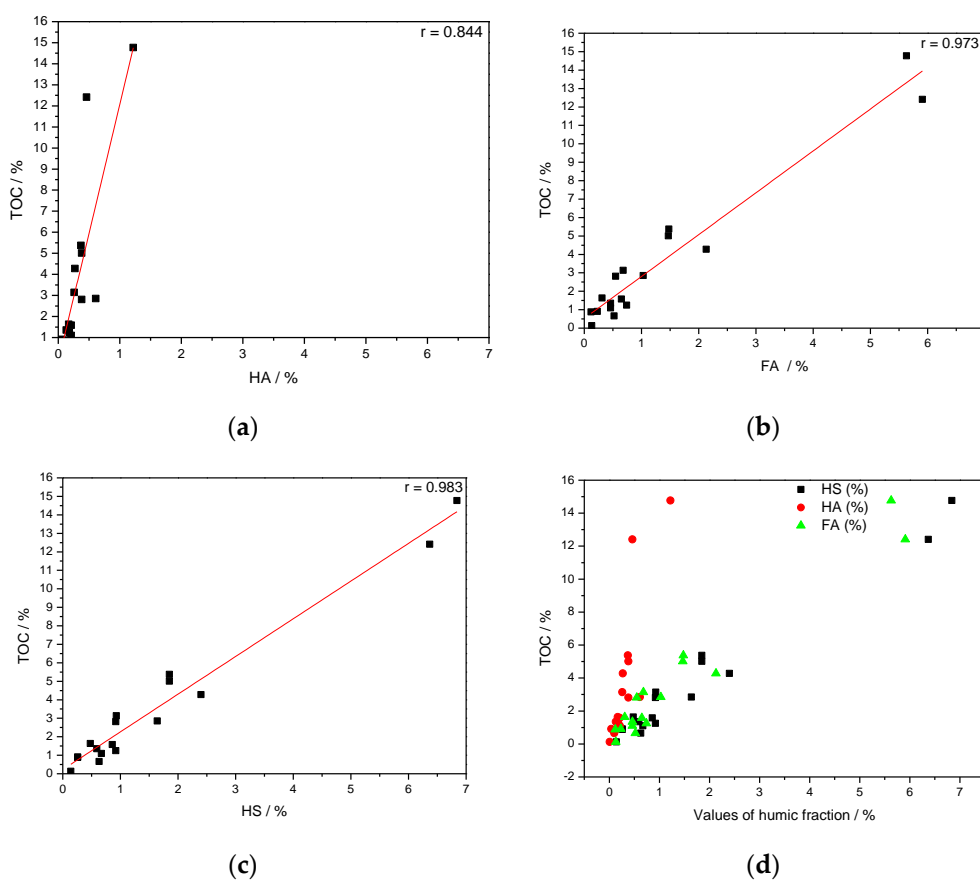
Figure 2. The studied correlation between TOC and humic fractions (**a**) TOC vs. HA, (**b**) TOC vs. FA, (**c**) TOC vs. HS, (**d**) TOC vs. HS, HA, FA.

One of the most important qualitative indicators of soil organic matter was the ratio C/N. As the value of TOC increased, the value of N_T also increased (see Figure 3).

Soil texture is a crucial factor involved in soil organic matter transformation processes. In terms of statistical processing, we compared the dependencies of individual values of the correlation between clay content and silt and sand values and silt vs. sand at separate soil sampling locations in selected profiles and soil types (see Table 5). In addition, the sand, silt, and clay representation affect transformation processes directly or indirectly through other factors such as pH.
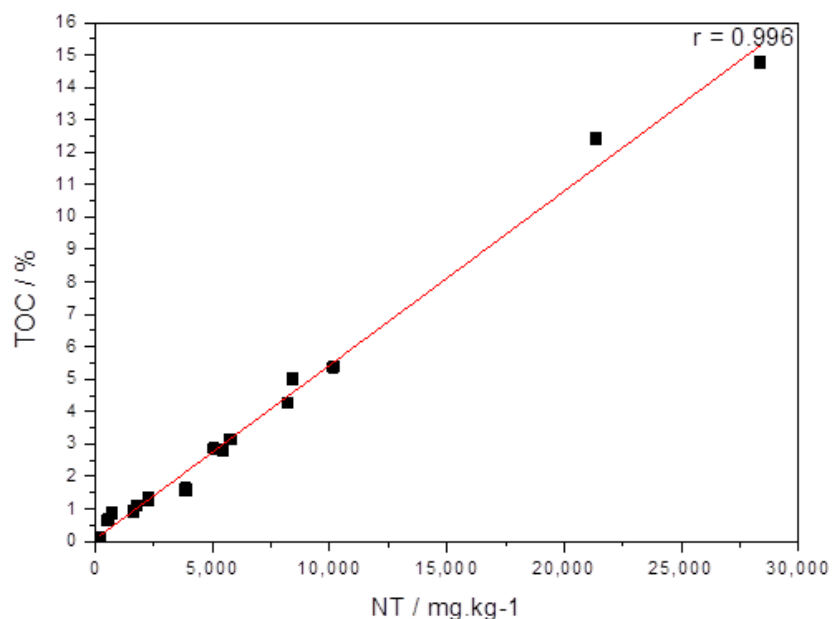
Figure 3. Studied correlation between TOC and total nitrogen content in soil profiles.

Table 5. Some characteristics of soils.

Profile	Depth [m]	pH(H₂O)	pH_KCl	Sand [a] [%]	Silt [b] [%]	Clay [c] [%]	Texture
P1	0.00–0.12	6.6	5.8	50.6	33,1	16.3	loam
	0.12–0.35	7.1	6.2	48.2	33.2	18.6	loam
	>0.35	7.3	5.7	43.3	16.3	40.4	clay
P2	0.00–0.07	5.6	5.0	45.6	30.9	23.5	loam
	0.07–0.36	5.7	5.1	45.2	7.4	47.4	sandy clay
	>0.36	6.0	5.3	48.5	4.1	47.4	sandy clay
P3	0.00–0.06	5.1	3.7	14.5	81.4	4.1	silt
	0.06–0.09	3.9	3.7	12.4	77.8	9.8	silt loam
	>0.09	6.0	4.4	45.6	4.6	49.8	sandy clay
P4	0.00–0.06	6.2	4.5	49.3	21.9	28.8	sandy clay loam
	0.06–0.20	6.1	4.2	45.5	5.3	49.2	sandy clay
	0.20–0.50	6.2	4.2	39.5	17	43.5	clay
	>0.50	6.1	4.1	19.4	16.7	63.9	clay
P5	0.00–0.15	6.4	4.8	38.3	26.9	34.8	clay loam
	0.15–0.30	6.2	4.4	43.5	6.3	50.2	clay
	0.30–0.60	6.0	4.1	16.6	4.3	79.1	clay
	>0.60	6.1	4.4	12.4	1.5	86.1	clay

P1–P5—soil profiles, pH(H₂O)—active soil reaction, pH(KCl)—exchange soil reaction, [a] 2–0.05 mm, [b] 0.05–0.002 mm, [c] <0.002 mm.

The measured values of the correlation coefficients of the textural fractions had an increasing character (see Figure 4).
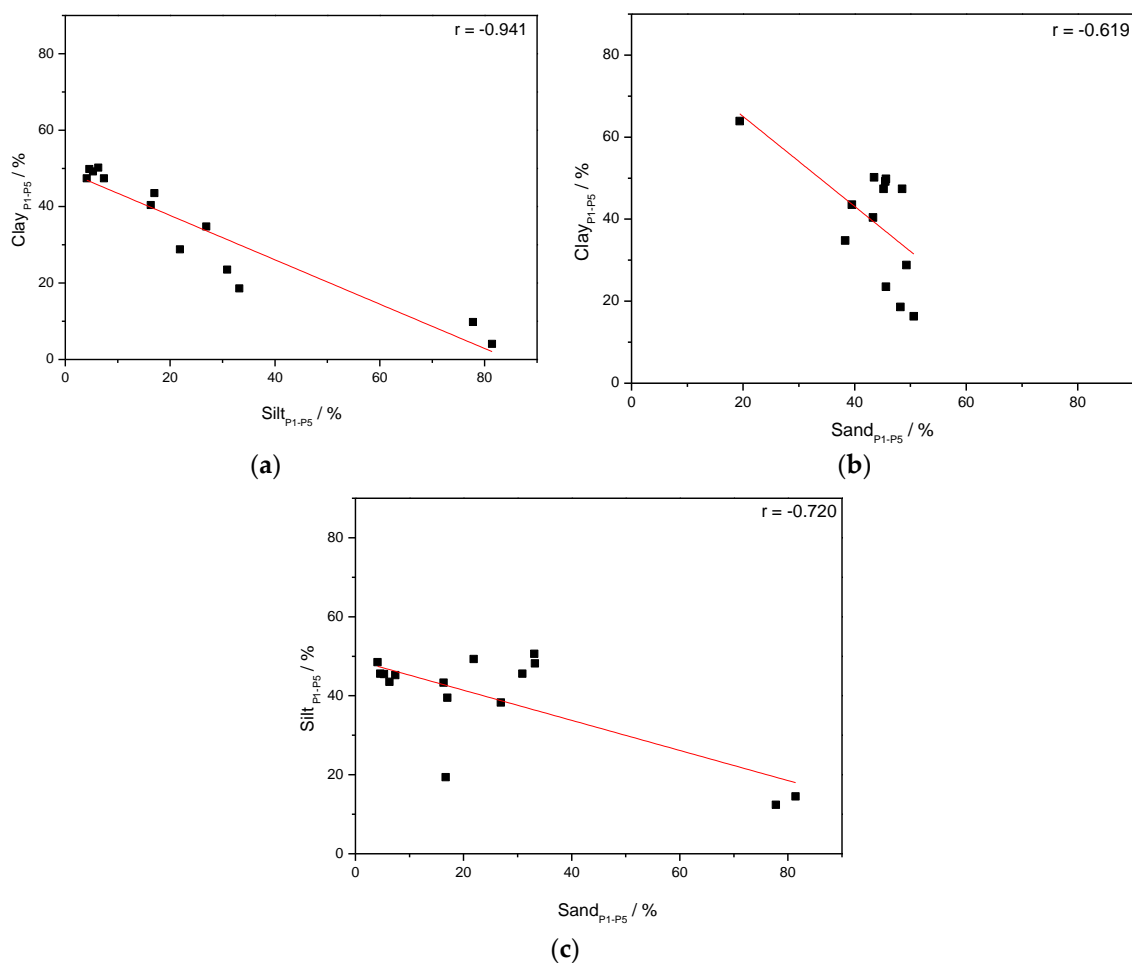
Figure 4. Studied correlation among textural fractions: (**a**) clay vs. silt, (**b**) clay vs. sand, (**c**) silt vs. sand in all soil samples.

We compared the values of correlation coefficients as summarised in Table 6. During statistical testing of the correlation relationship with the Spearman correlation, we found a correlation between total organic carbon (TOC) and soil texture fractions (silt, clay, sand).

Table 6. Correlation relationships between chemical factors of humus substances and textural characteristics in the soil.

Characteristics	pH_{H2O}	pH_{KCl}	Sand	Silt	Clay
TOC	−0.757 **	−0.521 *	−0.442	0.887 **	−0.650 **
HS	−0.795 **	−0.568 *	−0.516 *	0.864 **	−0.578 *
HA	−0.507 *	−0.496 *	−0.372	0.702 **	−0.500 *
FA	−0.813 **	−0.559 *	−0.521 *	0.861 **	−0.572 *
Q_{HS}	−0.804 **	−0.585 *	−0.469	0.774 **	−0.514 *
N_T	−0.728 **	−0.532 *	−0.432	0.877 **	−0.646 **
C/N	−0.080	0.305	0.189	−0.241	0.132
c(HA)/c(FA)	0.140	0.153	0.260	−0.315	0.165

* $p < 0.05$, ** $p < 0.01$, pH(H_2O)—active soil reaction, pH(KCl)—exchange soil reaction, TOC—total organic carbon, HS—humus substances, HA—humic acids, FA—fulvic acids, Q_{HS}—the colour quotient of humus substances, N_T—total nitrogen.

Although the Kremnica Mountains are a volcanic mountain range and their geolo-gical structure is based on lava bodies, the increased proportion of metallic elements in any fraction of humus substances was not analysed. Metallic elements in separate fraction soil samples from *Localities I–II* are summarised in Table 7.

Table 7. Contents of elements in separate fractions in three soil types (mg kg^{-1}).

	Fractions	Al	Ca	Cu	Fe	Mg	Mn	Zn	K
Andosol	HS	8.048	36.913	0.426	2.419	8.863	0.050	<D.L.	28.713
	HA	0.430	4.845	<D.L.	0.060	1.243	<D.L.	<D.L.	1.878
	FA	5.324	57.850	0.173	0.664	14.763	0.291	0.055	21.738
Cambisols	HS	2.070	23.482	0.184	1.410	5.773	0.178	<D.L.	14.364
	HA	0.050	2.359	<D.L.	0.003	0.497	<D.L.	<D.L.	0.778
	FA	1.049	42.701	0.084	0.069	9.131	0.136	0.183	14.938
Planosol	HS	3.844	30.333	0.235	3.106	7.333	0.038	<D.L.	12.419
	HA	0.039	1.820	0.006	0.002	0.365	<D.L.	<D.L.	0.585
	FA	0.939	40.735	0.115	0.125	8.154	0.204	0.060	14.029

<D.L. = below detection limit, HS—humus substances, HA—humic acids, FA—fulvic acids.

We observed the metal element dependencies in the HA fraction. The values of the correlation coefficients of Mg vs. Ca and K vs. Fe exceed the values equal to or higher than 0.9. In the HA fraction, the Ca content increased with increasing Mg content, and there was also an increasing pattern for K vs. Fe (see Figure 5).
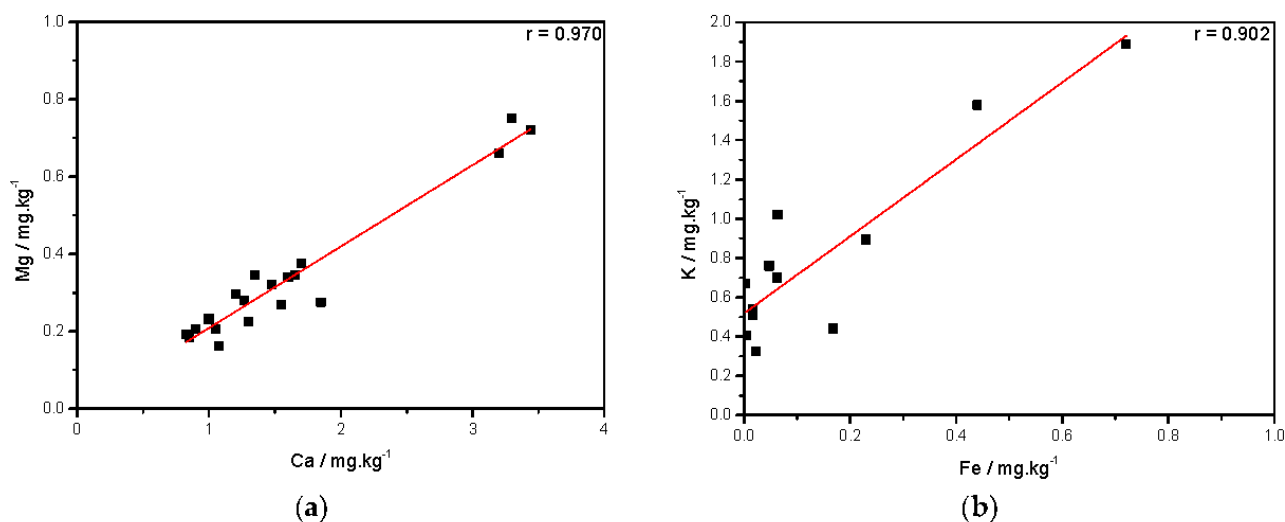

Figure 5. Studied correlations between metallic elements in the HA fraction (**a**) Mg vs. Ca and (**b**) K vs. Fe.

All studied metallic elements were more abundant in the fulvic than in the humic fraction (see Table 7). In the FA fraction, we found the following dependencies: Cu vs. Ca and Mg vs. Ca (see Figure 6a,b) and Mg vs. Cu (see Figure 6c).

In the FA fraction, we found the correlation coefficient of TOC vs. Fe had the value of r = 0.921 (see Figure 7).

(**a**)

(**b**)

(**c**)
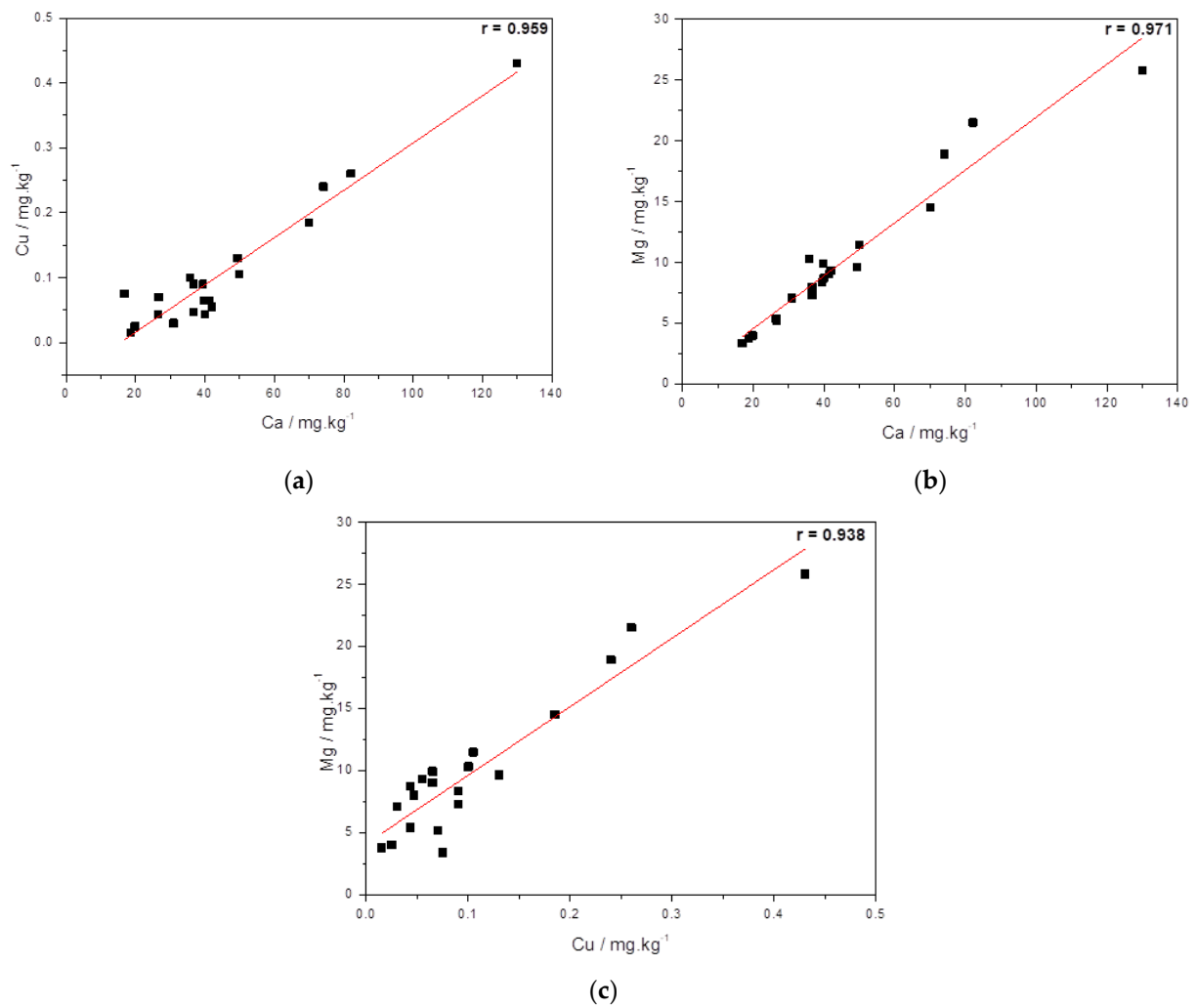
Figure 6. Studied correlations between the metallic elements in the FA fraction: (**a**) Cu vs. Ca, (**b**) Mg vs. Ca, (**c**), Mg vs. Cu.
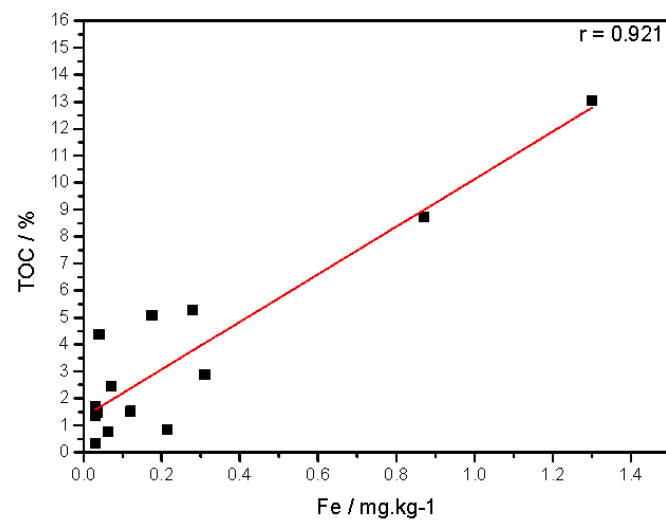
Figure 7. Studied correlation between TOC and Fe in the FA fraction.

4. Discussion

The soil samples under study ranged from a strong acidity to slightly acidic (pH(H$_2$O) = 5.70–6.19, see Table 3). The mean value in the Andosols (pH(H$_2$O) = 5.70) correlated with the observed values stated by the authors Gonzalez-Rodriguez and Fernandez-Marcos [64]. The exchange soil reaction of the Andosols was in the range of 3.86 to 4.61, and their acidic character formed of Al. The highest aluminium content also confirms this fact in this soil type. According to Barabasz et al., its most increased mobility is observed at pH = 4.00–4.50 [65].

The key factors are soil properties such as pH and clay, sesquioxide and organic matter content, and sorption/desorption/redox processes. They control the effectiveness of amendments for soil PTEs' immobilisation [18,66]. For example, soil colloids regulate the pH value in soil [66]. The highest mean content of humus substances was present in the *Andosol* soil type (xerothermic meadow), with an average value of 4.212% (see Table 3).

Andosols contain a substantial amount of humus substances with a relatively large surface area, leading to an increased capacity for the adsorption of various substances [67].

The authors Mishra and Sarkar [68] and Fabian et al. [69], in their studies, reported that the effect of different land uses (see Table 1) on soil organic carbon stocks was significant. The value of higher humus content may also be related to the pH values in *Andosols*. The differences in total soil organic carbon may be due to differences in biomass addition under different land-use practices, decomposition rates, and the different nature of plant materials [68]. In natural ecosystems, carbon stratification in the soil profile is a natural phenomenon, and TOC contents tend to decrease. The lower parts of the soil profile receive organic matter from leaching and siltation by soil fauna, dying roots, and root extrudates. The lowest value, 0.654% (see Table 3), was in the *Cambisol* soil type. Thus, humus substances extracted from the monitored soils indicate the low quality of humus, considering that the soils contain a high quantity of fulvic acids (see Table 4), which are more deficient in carbon than humic acid. The higher content of fulvic acids (cFA = 3.388%) in the analysed Andosol soil samples compared to humic acids (cHA = 0.823%) indicate a lower humus quality termed humate-fulvate humus.

The detected values of the colour quotient of humus substances indicate more humified and mature organic matter with a high presence of condensed compounds in the Cambisol and Planosol soil types (see Table 4). There was no significant difference in the humus substances´ quotient colour values between these two soil types. The average value of the colour quotient of observed humus substances in Cambisol was 2.26 to 2.71, and Planosol QHS = 3.10.

The highest average value of the colour quotient was observed in profile *P3* in the *Andosol* soil type in the xerothermic meadow, with a regular supply of dead plant debris forming the overlying organic horizon with different degrees of decomposition of organic matter on the surface of the soil. The higher value of the colour quotient is characteristic of low-humified, young humic acids with a fresh organic matter supply [70]. The use of land resources impacts the quality of humus substances in soil. The analysis shows that the *Andosol* soil type found in profile *P3* (*Eutric Andosols*) has many young humus substances at an early stage of humification. The absorbance at 465 nm, characteristic of these young humus substances, is highest for *Andosol*. The colour quotient values of humic acids were observed from 2.08 to 5.97 and for fulvic acids from 5.66 to 13.84 (see Table 4). These results do not correspond with the statement of Petrášová and Pospíšilová [71]. According to Petrášová and Pospíšilová, low values of the colour quotient are for humic acids (3–4) and high values for fulvic acids (9–10) [71].

The highest degree of condensation of the aromatic core, humification, and the quality of humus substances was observed in the *Planosol* soil type from a mowed meadow in profile *P1* (see Table 4). We found the lowest degree of humification in the *Andosol* soil type (*P3*) with the fresh supply of organic matter with the highest total organic carbon and humus substance content. It is characterised by a lower degree of aromaticity of humic acids (see Table 4). It follows that with a minor degree of condensation and dispersion of humus sub-

stances, the lower content of bioavailability forms of heavy metals decreased. It is primarily because humic materials consist of a skeleton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups. The major functional groups are carboxylic acid, phenolic and alcoholic hydroxyls, and ketone and quinone groups. Tsutsuki and Kuwatsuka [72] and Yonebayashi and Hattori [73] reported that the accumulation of humus substances in andic soils increases carbonyl- and carboxyl-groups, whereas alcoholic-, phenolic-, and methoxy-groups decrease concomitantly. According to Dube et al., the complexing ability of humic and fulvic acids results mainly from their content of oxygen-containing functional groups, such as the carboxylic (-COOH), phenolic (-OH), and carbonylic (>C=O) groups [74]. Chelate complexes are of preeminent importance. The humic and fulvic functional groups play a role as ligands. Each group may occupy two or more coordinating positions about metal ions and form closed rings. Humus substances of Andosol, mainly on the volcano substrate, are characterised by a high humification degree. Data on Andosol humus substances parameters indicate a low degree of humification for this soil type. Such values could be for forest floor (Ol diagnostic horizon) and not mineral soils. Higher values degree of humification of humus substances (HSs) are associated with a higher ratio of c(HA):c(FA) (see Table 4).

Our results confirmed that all humic fractions (HS, HA, and FA) increased with increasing TOC values. We found positive correlations among carbon parameters (TOC, HS, HA, and FA) in soil profiles (TOC vs. HS, r = 0.983; TOC vs. HA, r = 0.844; TOC vs. FA, r = 0.973; see Figure 2). As TOC values increased, HS, HA, and FA values increased too.

The total nitrogen content differences in soils often change from 0.05% to 0.5%. The arable land of most of the Slovak Republic is located at 0.1–0.2% of total nitrogen [75]. In soil samples of the investigated sites, N_T values for *Andosol* ranged from 28,350 mg kg^{-1} to 8225 mg kg^{-1}, for the *Cambisol* soil type from 10,150 mg kg^{-1} to 218 mg kg^{-1}, and Planosol from 5425 mg kg^{-1} to 1750 mg kg^{-1}. The values N_T decreased with increasing depth. Our results correspond with the study of Armas-Herrera et al., that demonstrate N_T values tended to be more abundant at 0–0.15 m depths than at 0.15–0.30 m depths [76]. The correlation coefficient among the TOC and N_T contents in soil samples from P1–P5 was r = 0.996, i.e., the correlation among the observed contents was very tight (see Figure 3).

Franzlubbers found high stratification ratios of soil C and N pools that could be good indicators of dynamic soil quality, independent of soil type and climatic regime [77]. In all soil types (*Andosol, Cambisol, Planosol*) at all monitoring localities, the TOC vs. N_T correlation value was above 0.9 (see Figure 3), i.e., the N_T value increases with TOC content. The total nitrogen content is different in soils, and in our soil's samples, the average value of C:N is reported to be 10–12:1 [78,79]. It correlates with the values found in *Cambisol* soil samples in soil profile *P2*. The highest values were in soil profiles *P1* and *P2*.

In terms of textural fractions in Table 5, we compared the dependencies of individual values of the correlation between clay content and silt and sand values and silt vs. sand at soil sampling locations in selected profiles and soil types.

As reported by Rodríguez-Bocanegra et al., the higher percentage of fine texture, dust, clay (loam), and organic matter in the subsoil (at root depth) may be one of the reasons for the lower concentrations of heavy metals in plant shoots [80]. In addition, clay (loam) can form strong bonds between the soil and heavy metals, making them less available to plants due to differences in biomass addition under different land-use practices, decomposition rates, and the different nature of plant materials [68].

During statistical testing using the Spearman correlation, we found a correlation between textural fractions in soil profiles *P1–P5*.

The correlation coefficient among the clay and silt contents in soil samples from Localities *P1–P5* was r = −0.941, i.e., the correlation among the observed textural fractions contents was very tight (see Figure 4a). Based on the results (see Figure 4b,c) of the statistical analysis, it can be stated that there was a significant degree of correlation among the clay and silt contents (r = −0.619) and a high correlation among the silt and sand contents

(r = −0.720) in soil samples from Localities I–II. The minus sign means that as the content of one element increases, the content of the other element decreases.

Based on analyses, TOC content was negatively correlated with clay fraction and positively correlated with silt fraction from Localities *P1–P5* (see Table 6). Among the TOC values, and silt content, the correlation coefficient was r = 0.887, which means that the correlation was high. Based on the value of the correlation coefficient among TOC and clay contents, r = −0.650 was a significant degree of correlation, which means that the TOC content decreases as the clay value increases (see Table 6). According to Jurčová and Tobiašová, the content of the total organic carbon is in positive correlation with the clay fraction [81], which does not correlate with our results. As reported by Burke et al. [82] and Bronson et al. [83], the fine fractions (clay, silt) are in a positive correlation with total organic carbon (TOC) and the coarse fractions (sand) in a negative. This statement corresponds with our results only in the case of TOC vs. silt. Based on our analyses, our clay fraction results were negatively correlated with TOC. The reason may be that a significant part of clay minerals is linked with many organic substances [84]. They can be stabilised through adsorption on the mineral surfaces [85], bridges of polyvalent cations [86], and binding into the interlayers of clay minerals [87].

Based on comparing the values of correlation coefficients in Table 6, the highest positive correlation coefficient value (r =0.887) was in TOC content vs. silt values. As the content of TOC increased, the values of silt increased too. The highest negative value of the correlation coefficient (r = −0.813) was FA content vs. pH(H₂O). As the value of FA increased, the value of pH(H₂O) decreased. Our results found that the silt fraction increased, and the clay fraction decreased with increasing TOC values.

4.1. Metallic Elements in Soil Samples

Order of elements in the fractions of humus substances for all samples at pH = 6 (Table 7):

(1) For humus substances (HS), the order of elements was for all soil types: Ca > K > Mg > Al > Fe > Cu > Mn

(2) For humic acids (HA), the order of elements was: Andosol: Ca > K > Mg > Al > Fe Cambisols: Ca > K > Mg > Al > Fe Planosol: Ca > K > Mg > Al > Cu > Fe

(3) For fulvic acids (FA), the order of elements was: Andosol: Ca > K > Mg > Al > Fe > Mn > Cu > Zn Cambisols: Ca > K > Mg > Al > Zn > Mn > Cu > Fe Planosol: Ca > K > Mg > Al > Mn > Fe > Cu > Zn

According to Tomaškin et al., the order of bioavailable elements in soil was [88]: Fe > Mn > Zn > Cu > Cr. Therefore, acidification of samples of the tested humus substances on the pH = 6 may be affected by bioavailable sorption forms of heavy metals in soil and bound heavy metal on the humus substance.

Metallic elements are brought into the soil primarily by human activity. However, some elements can come from rocks of volcanic origin. According to Delmelle and Stix [89] and Durand et al. [90], volcanic activity is responsible for the release of metals such as aluminium (Al), magnesium (Mg), copper (Cu), and zinc (Zn), among others. It must be taken into account that as soils become more acidic, these cations are replaced by H and Al [91]. This is particularly important in Andosols containing a high amount of Al [51]. The toxicity of Al occurs when pH is less than 5.5 [91], and this value is the borderline between acidic and slightly acidic soils. Soils of a volcanic origin, particularly *Andosols* [51], are known for their ability to store large contents of organic matter, which are attributed to the stabilization of soil organic matter in organo-metallic complexes, their association with short-range ordered minerals (allophane, imogolite, and ferrihydrite), and physical protection from microbial attack inside soil macroaggregates and microaggregates [92,93]. The monitored geological composition of the area represents volcanic rocks, mainly andesites, rhyolites, tuffs, and volcanic breccia. The geological footwall consists of lava flows of pyroxenic and pyroxene-amphibolic andesites. According to Ďurža, pyroxene and amphibole contribute significantly to the total content of elements (Mn, Cu, Zn, Co, Ni) in soils [94].

In their study, Li et al. found that human activities that altered the appearance of the landscape and the physical properties of the soil were crucial factors influencing soil contamination, especially for the risk elements Cu and Zn [95]. In compounds, the toxic effects between the particular metals can grow stronger (synergism Cd + Zn, Ni + Zn, Hg + Cu, and others) but also weaken (antagonism Se + Cd, Se + Hg) [96].

Similarly, Jiao et al. [97] and Wang et al. [39] found that anthropogenic activities could contribute about 41% of the accumulation of risk elements in agricultural soils. Copper and zinc are the main risk elements contributing to soil contamination. Rout and Das demonstrated an inhibitory effect of Zn on Cu where the intake of one element inhibited the intake of the other [98]. This may indicate the same mechanisms of the absorption of both metals. Nevertheless, the content of elements was not too high in any fraction of humus substances (see Table 7).

4.1.1. Metallic Elements Bound to HA and FA

We found the same order of metallic elements bound to soil humus substances in all soil types. The largest representation had calcium and potassium at an average of 27.54 mg kg^{-1} and 16.85 mg kg^{-1}, respectively. Zn and Mn content was not in the whole soil profile for all soil types in humus substances. The intake of Zn from the soil by plants is limited and depends the pH, the physicochemical properties of the soil, and the activity of microorganisms in the rhizosphere. Zn is absorbed by the roots mostly as a divalent cation (Zn^{2+}) [99]. The gleying process activates the reduced iron, manganese, and other elements, so the *Planosol* soil type had the highest iron content. In addition, Kostić et al. found a higher iron content in *Planosol* [100]. Mottling of sediments is most associated with redox processes, as is Mn staining, gleying and dissolution/degradation of ferruginous nodules, and types of Fe-oxide species present [101]. However, in *Cambisols*, soil type was not identified as Fe content in the whole soil horizon. Of the studied elements, only Zn was not found in humus substances. The order of elements in the humus substances was Ca > K > Mg > Al > Fe > Cu > Mn. However, this order does not accord with the argument of Chen et al., which claims that the sequence for some complexes of HS with divalent cations is as follows: Cu > Zn > Fe > Mn [102]. These differences may be caused by different soil types or the impact of the outside environment. A higher concentration of one specific element does not necessarily mean a higher degree of pollution or a higher ecological risk to health [103]. Approximately 22% to 66% of Cu in surface soil is mobile and is taken up by grass roots. In sandy surface soils, Cu uptake by roots (66%) is approximately twice as high as that of grasses (26%). Zn uptake by grass is approximately twice as high in sandy soils as in clay soils and twice as high as for Cu [104].

Heavy metals remain in the soil for long periods and have the potential to influence soil properties [105]. Their solubility in the soil is influenced by many soil chemistries, the most important of which are pH and organic carbon [106]. Many of these elements are relatively toxic to life, similar to lead [103].

4.1.2. Humic Acids

Humic acids form the highest quality component of humus substances [107]. For some elements in humic acids, there is an appreciable difference among the soil types (see Table 7). For example, the HA fraction for Cu (0.006 mg kg^{-1}) is only in the *Planosol* and not in the other soil types (*Andosol*, *Cambisol*). Copper in the soil is usually associated with anthropogenic sources such as industrial emissions or fertilisation [108]. Österberg et al. found that a prolonged dissolution rate characterised HA complexes formed with Cu, presumably because Cu ions diffuse into humic acid particles and bind to sites that may not be readily released [109]. It may be why Cu is only in the pseudogley soil type, where there is plenty of groundwater, which affects the gleying process.

The HA fraction of metallic elements tends to be higher in *Andosols* rather than in other soil types. According to Saeki and Kunito [27] and Saeki et al. [67], the negative charge of humic acid is expected to attract the risk elements' molecules to the surface electrostatically.

For some elements, Fe is the minimum content. However, the content of Zn and Mn was below the detection limit in the HA fraction in all soil types (see Table 7). The reason, it can be argued, is that complexes of humic acids with Zn contain few stables [110,111].

As the pH of solutions was similar among these humic acid samples, the differences in heavy metals adsorption were attributed to the intrinsic properties of the humic acids rather than the pH solution. The order of elements in the HA fraction was for the Andosol and Cambisols Ca > K > Mg > Al > Fe, but for the Planosol the order of elements was Ca > K > Mg > Al > Cu > Fe. According to Kerndorff and Schnitzer [112], the order of various elements on humus substances is as follows: Fe = Al = Cu > Zn > Mn.

Based on analyses, we found the dependencies among the selected elements to be increasing in nature. The correlation coefficient among the Mg and Ca contents was r = 0.970 and among the K and Fe contents was r = 0.902 in soil samples from HA fraction, i.e., the correlation among the observed elements was very tight. As the value of Mg increases, the value of Ca increases (see Figure 5a). Likewise, as the value of K increases, the value of Fe also increases (see Figure 5b). Unfortunately, the correlation coefficients of two elements (Mn, Zn) vs. metallic elements (Al, Ca, Cu, Fe, K, Mg) were not determined due to a lack of data.

We determined the correlations among selected metallic elements (Ca, Fe, Mg, K) and Al in the HA content. As the Ca, Fe, Mg, and K values increased, the Al values increased, and, conversely, as the Cu values increased, the Al values in the HA decreased. From the analyses obtained, the correlation coefficients presented had positive values, indicating that as the importance of Cu, Fe, and K increased, the values of Ca in the HA content increased. On the other hand, the correlation coefficients of selected metallic elements (Fe and K, Mg) with Cu decreased in the HA content. As Fe and K values decreased, Cu values increased. In the case of Mg vs. Cu dependence, the correlation coefficient had a positive value r = 0.474, which means a mild correlation degree. The correlation coefficient r = 0.854 represents the Mg vs. Fe dependence, e.g., the correlation among the contents of the observed elements was very tight. The correlation coefficient r = 0.831 represents the K vs. Mg dependence and was very tight too.

4.1.3. Fulvic Acids

All observed metallic elements (Al, Ca, Cu, Fe, K, Mg, Mn, and Zn) were found in the FA fraction (see Table 7). However, the order of elements in the FA fraction was different for all soil types (Section 4.1). The authors Schnitzer and Skinner indicate the following order of elements Zn > Fe > Mn > Mg [113], which does not correlate with the order of metallic elements as determined by the analyses. Hu et al. found that zinc was the most common element at risk in atmospheric deposition, followed by Pb > Cu > Cd [114]. In soil samples from FA only in the soil type of *Cambisol*, the Zn content was higher than the Cu content. In addition, Zn accumulation in soils is associated with transport (car tire wear—a point source of deposit).

Aluminium was shown to interfere with the uptake, transport, and use of Ca, Mg, P, and K [115]. However, we confirmed the correlation between Ca and Mg (r = 0.970) was very tight, and between Ca and K (r = 0.751) there was a high correlation in the FA fraction. Furthermore, we found a significant correlation (r = 0.604) between the Al and Mg contents in the FA fraction.

In the FA fraction, we found that as Cu concentration increased, Ca concentration also increased (r = 0.959). At the same time, as Mg concentration increased, Ca concentration also increased (r = 0.971), which means that the correlation was very high between the contents of the examined elements (see Figure 6a,b). The presence of high levels of copper in the soil can have many adverse effects on soil health. The limit value for copper (60 mg kg^{-1}) on permanent grassland was not exceeded at any of the sites monitored. However, high concentrations of Cu in soil significantly reduce soil urease and dehydrogenase activity and cause soil microbial communities to become resistant to Cu and antibiotics [116].

In the study by Wang et al., Cu and Zn concentrations in the surface soil layer exceeded the permissible limits of agricultural soils [117]. Neither Zn nor Cu exceeded the allowable limits in samples from land used as permanent grassland. The increase in the values for selected risk elements may be influenced by anthropogenic activities (roads, quarries, industrial and traffic emissions, and agriculture) [118]. It may also be due to the composition of the natural geological subsoil (parent rocks). Atmospheric deposition may have deposited these risk elements in the soil. In Figure 6c, in the FA fraction, as the Mg concentration increases, the Cu concentration also increases. The correlation among Mg and Cu (r = 0.938) was very high.

The correlations among the contents of the other elements were less than 0.7. Only among the Mg and Fe content was the value of the correlation coefficient r = 0.843, which means that the correlation was very tight among the contents of the examined elements. The correlation coefficients among the Mn and Fe content (r = 0.746) and K vs. Fe content (r = 0.706) had a high correlation.

4.2. Chemical Characteristics and Metallic Elements in Soil Samples

Our study relates to five soil profiles from two localities (Jastrabská vrchovina: *P1–P2* and Kunešovská hornatina: *P3–P5*), and three soil types, *Andosol, Cambisol,* and *Planosol*, were investigated.

Localities *P1–P2* and the *P4* soil type *Cambisol* were used as a moved meadow. The soil sampling in textural properties ranged from loam to clay (see Table 5). In the meadow ecosystem, the source of organic matter is mainly planting roots and their secretions, i.e., especially substances of a polysaccharide character [119]. The correlation coefficients of $pH(H_2O)$ vs. metallic elements in the HA fraction were less than 0.9. The $pH(H_2O)$ values vs. metallic elements (Al, Ca, Fe, K, Mg) were decreasing in nature except for $pH(H_2O)$ vs. Cu. The authors Yuanan et al. report that human activities probably had a significant impact on Cu content in agricultural soil [120]. When comparing the correlation coefficients of TOC vs. metallic elements in HA, only the value of the correlation coefficient of TOC vs. Cu had a decreasing character (r = −0.553).

In the FA, the values of the correlation coefficients of $pH(H_2O)$ vs. metallic elements were all decreasing in nature. Their values were lower than 0.9. The values of correlation coefficients of TOC vs. Al, Ca, Cu, Mg, Mn, Zn, and K were less than 0.9 in the FA fraction. The TOC values vs. Al, Ca, Cu, Mg, Mn, and K had an increasing character, while the TOC vs. Zn correlation value had a decreasing character. Only the correlation coefficient of TOC vs. Fe in the FA had a value of r = 0.921 and an increasing character (see Figure 7).

The analysed data decreased with depth in terms of carbon parameters (TOC, HS, HA, FA), and the highest values are in the surface layer. Wang et al. suggest that human activities can influence the concentration of risk elements [117].

TOC, FA, and N_T mean values for each monitoring locality were *P2 > P4 > P1*. The mean HS values for monitoring localities were *P2 = P4 > P1*. The mean HA values were *P4 > P2 > P1*. According to the content of selected elements (Al, Ca, Cu, Fe, K, Mg, Mn), their mean HS values for the localities were as follows: for Al and Fe *P4 > P1 > P2*; for Ca, Mg, K and Cu *P1 > P2 > P4*; and for Mn, they decreased *P4 > P2 > P1*. The pedogenesis of parent minerals is a long process, and the elements at risk in parent materials rarely move to the topsoil under natural conditions [121]. The authors Chai et al. reported in their study that among the risk elements investigated, Cu and Zn had a lithogenic source [122]. The correlation coefficient values among metallic elements (Al, Cu) vs. HS and HA did not exceed the values equal to or above 0.9 in *Cambisol*.

The *P3* locality soil type *Andosol* used as xerothermic meadow had textural properties ranging from silt to sandy clay. The analysed data decreased with depth in carbon parameters (TOC, HS, HA, FA) and N_T values. However, the values are two or more times higher when comparing the mean TOC values of the *Andosol* soil type with the Cambisol soil type. According to the content of metallic elements, the mean values in HS were as follows: Ca > K > Mg > Al > Fe > Cu > Mn and Zn were below the detection limit. The HA fraction of

metallic elements decreased in the same way, but below the detection limit were Cu, Mn, and Zn values. The mean values in FA were as follows: Ca > K > Mg > Al > Fe > Mn > Cu > Zn. The correlation coefficient values of metallic elements (Al, Cu) vs. HS did not exceed the values equal to or above 0.9 in *Andosol*.

The locality of *P5 Planosol* soil type used as mowed meadow had textural properties in the clay loam to clay interval (see Table 5). In terms of carbon parameters (TOC, HS, HA, FA) compared with *Cambisol* and *Andosol* values, the mean TOC value in the topsoil layer was identical to that of locality *P4*. According to the content of metallic elements (Al, Ca, Cu, Fe, K, Mg, Mn), the mean values of the analysed elements in HS were as follows: Ca > K > Mg > Al > Fe > Cu > Mn. It is the same as in the *Andosol* soil type.

In recent years, several studies have pointed out that atmospheric deposition is one of the significant contributors of large-scale risk elements to agricultural soils [123–127]. Therefore, a relatively wetter climate could influence more rapid soil profile development, i.e., leaching and concentration of elements bound in more resistant minerals [128]. In addition, it is difficult to find uncontaminated or pristine soils because industrial activities emit hazardous components and other contaminants into the air [129].

The correlation coefficients of metallic elements Al vs. C/N and Cu vs. HS did not exceed values equal to or greater than 0.9 in *Planosol*. The values of the correlation coefficients showed the dependence of Cu vs. C/N (r = 0.910) and Al vs. HS (r = 0.990), which, in both cases, increased with increasing C/N values.

5. Conclusions

The loss of soil organic matter from the soil has negative economic and ecological impacts on human society. Humus substances can improve unfavourable soil properties. In addition to its direct functions, soil organic matter also has ancillary effects (reduction of sediment transport, filtration of contaminants, biodegradation of contaminants, buffering of greenhouse gas emissions from the soil to the atmosphere).

The order of metallic elements in the HSs was Ca > K > Mg > Al > Fe > Cu > Mn. Only Zn was below the detection limit of the studied elements in humus substances. As the HS values increased, the metallic element contents (Al, Ca, Cu, Fe, K, Mg) also increased. In contrast to the increasing HS value, the value of Mn content decreased. The content of zinc was found only in the FA fraction when bound to the fulvic acids. The distribution of metallic elements among fulvic and humic fractions was mainly on the FA fraction. All studied metals (Fe, Al, Ca, Mg, K, Mn, Cu, and Zn) were abundant in the fulvic rather than in the humic fraction. In FA, all the values of the metallic element contents monitored were increasing except the value of Zn content. In humic fraction, the value of Cu content decreased with increasing HA values. The values of Mn and Zn were below the detection limit. In the cases where HA values increased, the metallic element (Al, Ca, Fe, K, Mg) contents also increased. The humus fraction in *Andosol* and *Cambisol* had metallic element contents of Cu, Mn, and Zn below the detection limit. Only the elements Mn and Zn were below the detection limit in the *Planosol* soil type.

The soil type *Andosol (xerothermic meadow),* located in Kunešovská hornatina Mts. (*Locality II*), contained higher concentrations of analysed metallic elements than other soil types such as *Cambisol* and *Planosol.*

Based on the analyses and calculated correlation coefficients, we found a very close relationship among K and Fe contents (r = 0.902, *p* < 0.01) in soil samples in the HA fraction. As K contents increased, Fe contents also increased. In the FA fraction, we found that with increasing Cu content, Ca content also increased (r = 0.959, *p* < 0.01). The correlation values among the contents of the analysed elements were very tight based on the calculated correlation coefficient. In both cases, as the values of one element increased, the values of the other elements also increased.

In the localities we surveyed, the HS value was in a positive correlation with the silt fraction (r = 0.864, *p* < 0.01) and in a negative correlation with the clay fraction (r = −0.578, *p* < 0.05) and the sand fraction (r = −0.516, *p* < 0.05). In addition, we found

positive correlations among HA and FA fractions and silt fractions (r = 0.702, *p* < 0.01; r = 0.861, *p* < 0.01). However, there were negative correlations among other fractions (FA and HA) and textural fractions (sand and silt).

This study suggests that a more detailed structural characterisation of metallic elements vs. soil humus substances may represent a helpful parameter for differentiating among soils of volcanic origin. This study's results can help illustrate the distribution of metallic elements among the fractions of humus substances in soil with a clear expected future for further applications.

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