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MATRIX CHARACTERIZATION AS A TOOL OF INVESTIGATION OF RISK HEAVY METALS BEHAVIOUR IN THE ENVIRONMENT

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In this paper the matrix characterization of chosen solid environmental samples and assessment of its impact on the association of risk metals with mineral phases of these samples, which makes their mobility in the environment, is presented. Results of X-ray diffraction analysis, determination of total carbon contents (TOC, TIC) and constituent elements have confirmed differences in the mineralogical composition of samples. In the soil and sediment samples, more than 80 % content of mineral forms of silicon and silicates was determined, moreover sediment contains also carbonates. In the sample of gravitation dust sediment (GDS), high (approx. 80 %) content of amorphous material was determined. The rest was formed from a wide variety of minerals. In comparison with two other samples under study, amount of GDS in the environment is least, but in spite of this it significantly influences input of heavy metals to the soils, particularly in the industrial areas.

Key words: heavy metals in the environment, matrix characterization, environmental analysis, gravitation dust sediment, soil.

Karakterizacijska matrica kao alat za istraživanja toksičnog djelovanja teških metala u okolišu. U ovom radu predstavljena je karakterizacijska matrica izabranih čvrstih uzoraka iz okoliša te je procijenjen utjecaj tih uzoraka na poveznicu toksičnosti metala sa sastavom minerala koja određuje mobilnost metala u okolišu. Rezultati rendgenske difrakcijske analize, određivanja ukupnog sadržaja ugljika (organskog, TOC i anorganskog, TIC) i građevnih elemenata potvrđuju razlike u sastavu minerala u svim uzorcima. U uzorcima tla i sedimenta više od 80 % sadržaja čine mineralne forme silicija i silikata dok sediment sadrži i karbonate. U uzorcima sitnih čestica dobivenih gravitacijskom sedimentacijom (GDS) određen je visoki (oko 80%) sadržaj amorfnog materijala. Ostatak pripada različitim minearlima. U usporedbi s druga dva uzorka u ovom istraživanju, količina GDS u okolišu je manja, ali unatoč tome utjecaj unosa teških metala je značajan, posebice u industrijskim područjma.

Ključne riječi: teški metali u okolišu, karakterizacijska matrica, analiza okoliša, gravitacijska sedimentacija sitnih čestica (GDS).

INTRODUCTION

The issue of environmental protection results from requirements of present modern time. Global industrialization, urbanization and intensive soil management have brought positive results, but on the other hand they have had also negative impact on the all parts of the environment (water, soil, sediment, atmosphere, vegetation) in consequence of a rapid increase in the heavy metals content [1, 2]. The environment and human, as its part, are attacked by different pollutants/risk substances, from which heavy metals have significant position. In terms of prevention and protection of the environment is important to know not only the state of its basic components but also character of undesirable products of anthropogenic activities significantly influencing this state [3]. Pollution by heavy metals is a serious problem due to their toxicity, bioavailability and non-biodegradability in the environment [4].

Metals are present in the environment due to natural processes as part of mineral materials of solid components, and due to anthropogenic activities as part of dust particles emissions [1] from vehicle or combustion of coals, industrial wastes, dry and wet precipitation of other pollutants [2]. One of the approaches enabling responsible assessment of anthropogenic activities impact on the environment and fate of the risk substances/heavy metals in him, is utilization of adequate methods of analytical control of cycle of risk elements in the environment. The main transport media providing movement of heavy metals between solid components of the environment and within themselves, represent atmosphere and water (surface water, groundwater, soil water, etc.). The behaviour of heavy metals in the environment depends on their chemical form, type of the binding or associations with different phases of the matrix of environmental samples [3]. Considering the continual cycle of elements in the environment, the study of element mobility in the solid environmental samples is highly up-to-date. The solid environmental samples are not only solid components of the environment but also unacceptable solid products of industrial activities, which represent potential source of the environmental pollution [5, 6]. Regarding their different origin and position in the environment it is possible to presume their different properties and behaviour in the environment. The mineralogical composition and content of organic and inorganic matter are very significant properties of these solid environmental samples, which matrix consists of inorganic and organic material. The behaviour (bioavailability, mobility, toxicity and distribution) of risk elements in the solid environmental samples depends not only on their total content, but also on their chemical forms or type of the binding in the samples and therefore the determination of the total element content in these samples does not give sufficient information about pollution of the environment [6, 7, 8]. The sediments and soils are very often monitored components of the environment because accumulation of risk elements in them causes a potential risk to human health due to transfer of these elements in aquatic media, their uptake by plants and subsequent input to the food chain [5]. Therefore the contamination of soils by risk elements represents a serious environmental problem and has significant connection with human health. It is important to mentioned, that elements from anthropogenic sources tend to be more mobile in soils than those from natural (pedogenic or lithogenic sources [9].

The solid industrial wastes (ash, fly ash, emissions of solid pollutants) very often contain variable content of toxic or potentially toxic elements (risk elements), which may be dangerous for the environment and human. The emitted solid pollutants become part of the atmospheric dust particles. The atmospheric dustiness can be divided, from the ecological point of view, into two groups: the gravitation dust sediment (GDS) and the fly ash. The gravitation dust sediment is created by particles with high sedimentation ability [10]. Soils are frequently place of settling of dust particles and risk element forms, which are able to release from dust particles during given soil-ecological conditions, and may them contaminate.

To better assess of associations of metals with matrix phases of solid environmental samples and thus their biological activity, toxicity, mobility and long-time exposure to the environment, determination of total element content is not sufficient [11]. Namely this information do not allow a full assessment of the environmental impact of polluted soils or sediments because they can be present in different chemical forms (easily exchangeable ions, metal carbonates, oxides, sulphides, organometallic compounds, ions in crystal mineral lattices etc.) with variable mobilization capacity and bioavailability [4]. As already mentioned above, distribution, mobility and biological bioavailability of elements depends not only on their content in the environment, but first of all on their chemical and physical state. Changes in the environmental conditions, natural or anthropogenic, have significant impact on the behaviour of essential and toxic elements that may change the forms of their occurrence. To understand the environmental chemistry of the given element is necessary to characterize all its forms in the various possible conditions of natural systems in their entirety. Since this approach is practically impossible, to clarify the transformations between different forms of element, it is effort to characterize at least its the most important forms of occurrence.

Following these information, it is possible to assess probable environmental consequences [12, 13]. Here is scope for application of methods of fractionation analysis, which allow the classification of element forms with different mobility in the environment given by the nature of transport medium. Submitted paper represents part of the extensive experimental study focused on the optimization and application of fractionation analysis procedures for solid environmental samples (soils, sediments, gravitation dust sediment). The results of the fractionation analysis take the wider dimension in the context of the study of basic chemical properties given environmental samples, characterization of constitution of their basic structural matter (matrix) and assessing its impact on the association of risk elements with mineral phases of these samples, which underlie their mobility in the environment, that is the aim of this contribution.

MATERIALS AND METHODS

Three types of solid environmental samples (agricultural soil, lake sediment and gravitation dust sediment – GDS), collected in the locality Košice (residential city agglomeration) and Košice – surroundings, were used for our study. The soil and sediment samples are of the same origin but different position in the environment. The soils are exposed to the direct intervention of agricultural activities and contact with atmospheric oxygen. The sediments play an important role in the distribution of metals in the water ecosystems. GDS, in spite of its minority interest in the environment, is a typical representative of pollutants of anthropogenic origin and one of the possible sources of risk entry metals into the soils.

Sampling

The soil samples (P1 – P4) were collected from four well-chosen sampling sites near the metallurgical plant U. S. Steel Košice to the polyethylene bags. Sampling site P1 is situated near the waste dump management of metallurgical concern, locality P2 is near the wastewater treatment plant, locality P3 is located in direction of prevailing winds and locality P4 in close proximity to the concern. Sampling of soil samples was performed using the spade to the depth of 20 – 25 cm (horizon A). Sampling sites of the partial samples were selected so, the gross sample represented corresponding sampling locality. Individual soil samples were after sampling dried at laboratory temperature and after removing of vegetable rests quartered. After quartering were cemented parts of skeleton crushed in the agate mill and then was sample sifted through a sieve brass with aperture size 0.2 mm.

Samples of lake sediment were collected from the water reservoir Domaša (East Slovakia) and they represent its different areas. Sample S1 – entrance to the reservoir, samples S2, S3 – centre of the reservoir, S4 – output from the reservoir. Sampling of sediments was realized using tube core barrel sampler triggered by gravity. The length of the core was approx. 40 cm (S2, S3), respectively 30 cm (S1, S4). Final sample from each sampling site was prepared by mixing of four individual samples. After collection, the samples were dried and homogenized by grinding in the agate mill.

Sample of gravitation dust sediment (GDS) comes from locality Košice-city and was collected for three years in one liter glass-settling vessels replete by 250 cm^3 of distilled water. After expiration of the exposition time, the content of vessels was quantitatively flushed by distilled water into the pre-weighed evaporation Pt-dishes in a water bath and evaporated to dryness. The dried residue was further homogenized by crushing and grinding in the agate mill.

Matrix characterization

The study of the matrix of samples was designed to determine the phase composition, determination of total organic carbon (TOC), total inorganic carbon (TIC) and significant elements of matrix. The method of X-ray diffraction analysis (XRD) was applied for investigation of mineralogical (phase) composition of the studied samples (fully automatic difractometer URD-6, Rich. Seifert – FPM, Germany, radiation - CoKα/Ni filter, voltage - 40 kV, current intensity - 35 mA, step 0.05 ◦2θ). The internal standard (cca 5 weight % of chemically pure ZnO – zincite) was added to the sample for purposes of quantification of the amorphous material. The scanning electron microscopy with X-ray microanalysis (SEM-EDS) using electron scanning microscope TESCAN VEGA TS 5130 LM with energy-dispersive microanalytic spectrometer OXFORD INCA Energy 350 provided information about elements composition of the particular place of the particle surface. TOC and TIC was determined by element analysis (Analytic Jena - multi N/C 3100, with thermocatalytic oxidation and MCNDIR detection for TOC analysis). The total content of element was performed by Wavelength Dispersive X-ray Fluorescence (WD XRF) analysis using equipment Spectroscam MAKC – GV, Russia.

Chemical properties of soil

Soil water, respectively soil solution, is responsible for the transport of elemental forms of dust sediments into soils, from soils into vegetation as well as it is the transport medium of elements between soils and sediments. For this reason, chemical properties of soils affecting the mobility of elements in the soil system (soil reaction and indicators of sorption capacity of soils) have been investigated. Selected chemical properties of soils were determined using methodology valid for this type of analysis [14].

Determination of active soil reaction (pH_{H2O}), respectively exchange soil reaction (pH_{KCl}) was carried out by potentiometric analysis in the extract of suspension sample/boiled distilled water, respectively sample/0.1 mol dm^{-3} KCl.

Hydrolytic acidity (HA) was calculated from the results of acetic acid titration resulting after displacement of H^+ and Al^{3+} ions from the sorption complex of sample by solution of hydrolytic basic salt (1 mol dm^{-3} CH_3COONa). The amount of exchange basic cations (S) was determined by titration with HCl resulting after displacement of exchange cations. 0.1 mol dm^{-3} NaOH was used for titration in both cases. The sum of results of both determinations represented cation sorption/exchange capacity (T) expressed in mmol kg^{-1}. Sorption saturation, respectively saturation degree of the sorption complex (V) was expressed as a percentage of the amount of exchange cations with respect to sorption capacity representing 100 %.

RESULTS AND DISCUSSION

Samples of soils, sediments and GDS were analyzed in order to identify the phase composition of the matrix (XRD), total organic and inorganic carbon (TOC and TIC analysis), and the total content of significant matrix elements (WD XRF). The results of these assays provide us with information about the chemical composition of the matrix of the studied samples.

Matrix characterization

The percentage of mineral phases and amorphous material in the studied samples obtained by XRD analysis is indicated in Table 1. The results of analysis pointed to the different composition of the matrix of the studied type of environmental samples, that reflects their different origin and status in the environment.

In the samples of soils (P1 - P4) and sediments (S1 - S4) was confirmed more than 80 % presence of mineral forms represented by quartz (soils approx. 40 - 48 %, sediment approx. 33 - 40 %), aluminosilicates (soils approx. 34 - 46 %, sediment 40 - 48 %) and in case of sediment also by carbonates (approx. 2 - 6 %). Representation of mineral forms of aluminosilicates in soils decreases in the order: clay minerals - muscovite (about 19 - 24 %), plagioclase albite (about 7 - 17 %), chlorite (about 2.5 - 9.5 %), feldspar - orthoclase (2 - 4 %). The highest content of quartz was determined in the soil P2 and the lowest in the soil P4. Soil P3 was characterized by the highest amount of amorphous material and in comparison with other samples of soils it had the lowest content of aluminosilicates. On the basis of determined composition it is possible our samples of soils classify as neutral soils, respectively as soils with predominant neutral minerals. The mineralogical composition of some chosen above mentioned samples is shown in Table 1.

Table 1. Matrix composition, total content of matrix elements, TOC and TIC of individual samples
Tablica 1. Matrica sastava, ukupni sadržaj elemenata matrice, ukupni organski ugljik (TOC) i ukupni anorganski ugljik (TIC)

Component/Sample	Content [weight %]								
	P1	**P2**	**P3**	**P4**	**S1**	**S2**	**S3**	**S4**	**GDS**
Quartz	45.00	48.12	47.08	39.36	36.29	33.70	35.82	41.50	7.51
Muscovite 2M1 (K)	21.10	19.10	21.80	24.20	27.80	34.80	28.60	17.20	2.61
Plagioclase Albite (Na)	14.67	17.36	6.84	9.60	5.32	5.51	9.46	10.67	-
Chlorite IIb-2 (Mg, Fe)	6.90	2.49	2.96	9.50	3.63	3.83	5.02	-	2.94
Chloritedis (Mg, Fe)	-	-	-	-	-	-	-	12.39	-
Orthoclase (K)	3.80	3.56	2.27	3.28	3.89	3.59	-	3.63	-
Anorthoclase	-	-	-	-	-	-	3.08	-	-
Magnetite	-	-	-	-	-	-	-	-	3.47
Hematite	-	-	-	-	-	-	-	-	3.41
Calcite	-	-	-	-	3.57	3.38	1.86	2.27	1.21
Dolomite	-	-	-	-	2.34	-	-	-	0.68
Amorphous	8.60	9.30	19.00	14.10	17.20	15.20	16.20	12.30	78.17
Element/Sample	**P1**	**P2**	**P3**	**P4**	**S1**	**S2**	**S3**	**S4**	**GDS**
Si	31.53	33.39	34.12	32.60	29.14	28.90	29.80	30.56	7.11
Al	7.77	6.24	6.09	7.58	7.29	7.72	7.34	7.35	2.25
Fe	2.70	2.99	2.86	3.48	4.28	4.24	4.50	3.98	7.69
Ca	0.55	0.46	0.61	0.45	1.91	1.99	1.24	1.55	1.63
K	1.29	1.04	0.93	1.21	1.12	1.15	1.16	1.12	0.23
Mg	0.60	0.60	0.50	0.60	0.93	0.92	0.93	1.10	1.56
TOC	1.50	1.76	1.41	1.09	0.90	1.24	1.14	1.23	34.93
TIC	0.08	0.10	0.17	0.43	0.67	0.76	0.51	1.20	5.81

A lower proportion of quartz in the samples of sediments (S1 to S3) opposite samples of soils was balanced by higher proportion of muscovite. The results further indicate that sediment sample S4 (output from the reservoir) has a slightly different character than the other samples. It is the richest in quartz content at the expense of the lowest content of muscovite. It is only sample with content of mineral chloritedise (similar to chlorite) and it has the lowest content of amorphous material. Representation of clay minerals plagioclase and chlorite was in soils and sediments approximately the same and dependent on the location of sampling. The similarity of mineralogical composition of soils and sediments reflects a common origin of these environmental components.

Results of mineralogical composition of GDS from Košice residential city agglomeration showed the difference of this sample from previous samples of soils and sediments. While in soils and sediments were predominant mineral forms (80 % / w/w), in the samples of GDS (Table I) it was amorphous material (80 % / w/w). Mineral share consists of various minerals like quartz (approx. 7.5 %), iron oxides (approx. 7.0 %), silicates (approx. 5.5 %) and carbonates (approx. 2.0 %). Presence of iron oxides, noticed only in this sample, relates with the fact, that composition of GDS in the industrial regions reflects source of dust particles in the environment – metallurgical production. In soils, which are place of fall of these particles was iron incorporated into the matrix of aluminosilicates (Chlorite). From all studied samples, sample of GDS had the most various representation of mineral forms in spite of this, that they created only 20 %.

SEM-EDS analysis has confirmed the largest share of Fe oxides and barite particles. There were about 20 individual particles of this phase and 6 clusters of different scale. The largest one is shown in Fig. 1. There were also found approximately 10 Cu sulphides particles and about the same number of chalcopyrite particles. Analysis has confirmed presence of particles with Pb content (Fig.2). Randomly were found following particles: phosphates of lanthanides, yttrium phosphate, particles of brass, Pb-Sn, and Sb-Fe-Cu. SEM picture (Fig. 3) demonstrates scale and shape heterogeneity of some part of GDS sample.

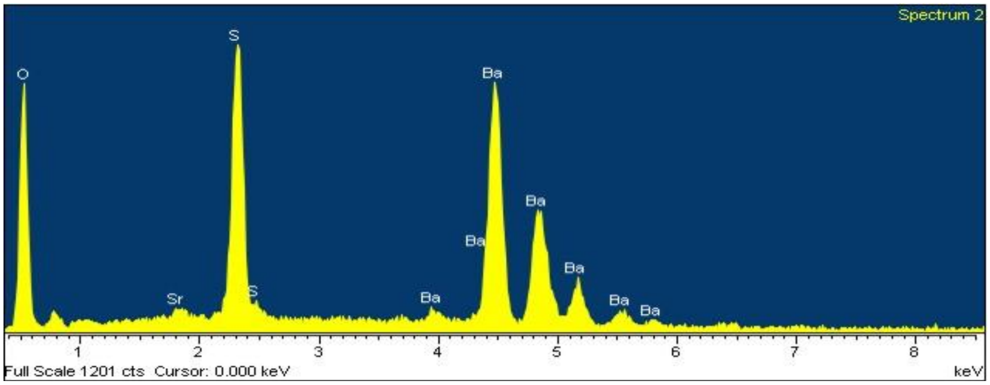

Figure 1. X-ray spectrum of some barite particles in GDS sample
Slika 1. Spektar rendgenske difrakcijske analize baritnih čestica u GDS uzorcima

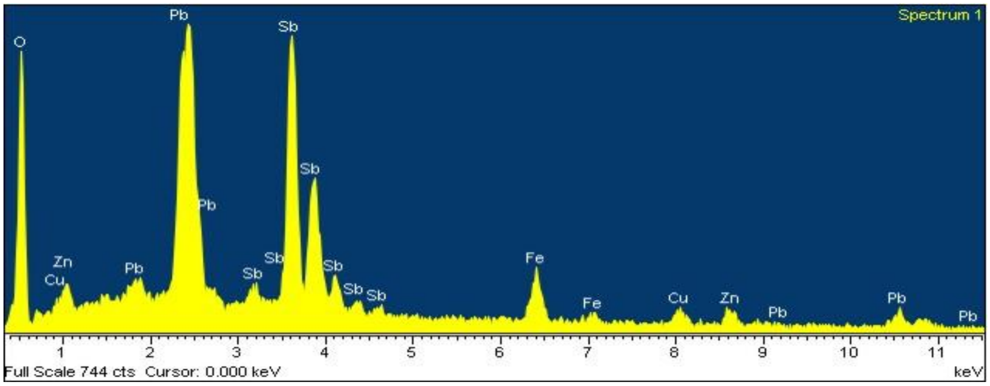

Figure 2. X-ray spectrum of some Pb, Fe, Cu, Sb particles in GDS sample
Slika 2. Spektar rendgenske difrakcijske analize Pb, Fe, Cu, Sb čestica u GDS uzorcima

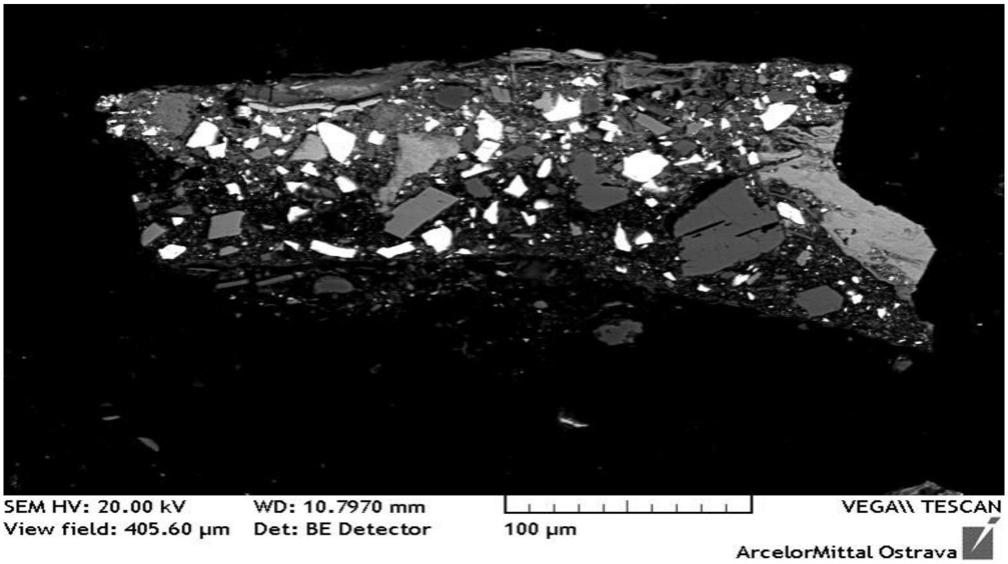

Figure 3. SEM picture of some part of GDS sample
Slika 3. Rezultati skenirajuće elektronske mikroskopije (SEM) dijela GDS uzorka

Total content of main elements and carbon

Total contents of main components, organic and inorganic carbon can be used for confirmation of results of phase analysis of matrix. Table 1 shows total contents of Si and Al (part of aluminosilicates), Fe contents (part of Chlorite, Chloritedise, Hematite, Magnetite), Ca (part of Calcite), K (part of Muscovite, Orthoclase, Anorthoclase), Mg (part of Chlorite, Chloritedise, Dolomite), TOC (part of organic material) and TIC (part of carbonates).

The results of determination of total content of matrix elements in studied samples correspond to the results of mineralogical composition determination of their matrix. The highest content of silicium and aluminium correspond to the highest content of quartz and aluminosilicates in the samples. Determined contents of iron and magnesium have connection with presence of chlorite (chloritedis) in the samples and higher content of iron in the sample of GDS has also connection with magnetite and hematite. Determined potassium in the samples confirmed presence of muscovite and orthoclase minerals. The lowest potassium content was detected in the GDS sample where presence of orthoclase was not noticed and muscovite had only low abundance in the sample. Higher calcium content in the sediment and GDS samples than in the soil samples confirms presence, respectively absence of carbonates in the studied samples.

The results of the total content determination of both types of carbons indicate that TOC in the samples decreases in the order: GDS, soil, sediment and TIC in order: GDS, sediment, soil. TOC in the GDS was about 30 times higher than in the samples representing components of the environment (soil and sediments) and corresponds to the presence of organic matter in an amorphous material. Low content of inorganic carbon in the soils confirms the fact, that unlike the sediments and GDS, presence of carbonates was not confirmed in these samples.

Found phase (mineralogical) composition, supplemented by the results of total contents determination of matrix elements, organic and inorganic carbon in the studied solid environmental samples confirmed presumption of difference of basic building material (matrix) of these samples which relates with their different origin and position in the environment. Different matrix composition influences also different way of binding of these elements in the studied samples and so their different mobility under certain ecological conditions. Selection of extraction reagent suitable for evaluation of elements mobility at a moderate change of ecological conditions (mobilizable fraction) is conditioned by presence of carbonates or organic matter in the sample. To isolate metals associated with carbonates is used 16-hours extraction of 0.43 mol dm^{-3} CH_3COOH and 1-hour extraction of 0.05 mol dm^{-3} EDTA for metals bound in the organic matter. Regarding to absence of carbonates in the soil samples, use of time-consuming CH_3COOH-extraction would be useless, therefore for mobility assessment suffices EDTA-extraction. Carbonates and organic material occur in the matrix of sediment samples in the comparable contents, what is an assumption of extractability of metals to both extraction agents. Presence of carbonates and organic matter was also proven in the GDS. Regarding to dominating content of organic carbon against inorganic carbon it is expected significantly higher extractability of metals from GDS to EDTA than CH_3COOH extraction reagent.

Chemical properties of soil

Selected parameters characterizing chemical properties of soils are in numerical and verbal form presented in Table 2.

Following chemical analysis results can deduce, that soils P1, P2 and P3 belong to the neutral soils and P2 soil to the weakly acidic soils. This is in accordance with low calcium and magnesium content in soils and the absence of carbonates, the presence of which would lead to the pH increasing to the alkaline area. Decreasing of pH of soils supports heavy metals mobility, which can more easily get into agricultural plants and therein into the food cycle.

Cation sorption capacity relates with organic matter content and clay fraction in the soils. Lower TOC content in P4 soil, compared to other, was reflected in a reduction in sorption capacity.

On the basis of the found values of sorption capacity indicators, particularly the degree of sorption complex saturation, which is excepting P2 soil fully saturated, we suppose, that may occur exchange of the original ions, Ca^{2+}, Mg^{2+}, K^{+}, NH_4^{+}, Na^{+} from the soil sorption complex for ions of risk elements and thus partially them immobilize under normal conditions. Contrary, under changed conditions, these ions can be mobilized again by stronger interactions with organic complexes.

Table 2. Parameters characterizing chemical properties
Tablica 2. Kemijski parametri ispitivanih uzoraka tla

Soil sample	pH_{H2O}	pH_{KCl}	HA [mmol kg^{-1}]	S [mmol kg^{-1}]	T [mmol kg^{-1}]	V [%]
	Numerical expression					
P1	7.09	6.78	14.06	205.83	219.88	93.61
P2	5.73	5.41	33.38	186.75	220.14	84.84
P3	6.63	6.53	12.30	216.87	229.17	94.63
P4	7.19	6.77	9.22	155.63	164.82	94.42
	Verbal expression					
P1	neutral	neutral	very strong	-	upper midle	fully saturated
P2	weakly acid	acid	very strong	-	upper midle	saturated
P3	neutral	weakly acid	strong	-	upper midle	fully saturated
P4	neutral	neutral	strong	-	lower midle	fully saturated

CONCLUSION

On the basis of obtained results, following conclusions can be deduced from this part of experimental work:

a) determination of the phase composition, total content of the matrix elements, TIC and TOC confirmed, that the composition of the matrix of the studied samples is different to one another depending on their origin and the position in the environment,
b) gravitation dust sediment, in comparison with two other studied samples, is present in the environment in the minimum quantity, but in spite of this, thanks to diversity of its matrix and high organic content, it may significantly affect the entrance of heavy metals into the soils, particularly in the industrial areas,
c) selected chemical parameters of the studied soils samples indicate the possibility of increasing the mobility of elements in case of changed soil conditions,
d) different properties of the matrix of solid environmental samples also affect different mobility of elements in the environment.

Mentioned conclusions are an important information source and basis for the mobility study of selected risk elements (Cu, Ni, Pb, Zn) in the given samples by fractionation analysis.

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