Ultrasound-assisted extraction of matrix elements and heavy metal fractions associated with Fe, Al and Mn oxyhydroxides from soil

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Abstract: Single agent extractions of major and trace metals from soil samples were conducted by means of a rotary mixer and an ultrasonic bath with sonication times of 10, 20, 30, 40 and 50 min. The sequential extraction was undertaken according to the European Community Bureau of Reference. The obtained soil extracts were analyzed by inductively coupled plasma-optical emission spectrometry and according to the results, the rotary mixer-assisted extraction was more efficient in the case of alkaline earth elements. However, by use of ultrasound, several times higher amounts of matrix elements (Fe, Al and Mn) and heavy metals predominantly associated with Fe, Al and Mn oxyhydroxides were extracted. The increase of the sonication time failed to improve the extraction yields. The changes in the conductivity, pH, redox potential, particle size diameter and zeta potential of colloid particles with increasing sonication time were measured. The extraction mechanism and expressed selectivity of ultrasound is discussed and an explanation is suggested.

Keywords: soil analysis; extraction mechanism; sequential extraction; soil phases.

INTRODUCTION

The measurements of major elements in soil samples are required to expand knowledge of the elemental composition of soil, while the assessment of the soil trace metal content is of major importance nowadays, due to their toxic effects and bio-accumulative nature. An excessive presence of metals in soils and sediments of industrial regions, particularly, and their potential leakage into surface and groundwaters could pose environmental problems. Thus, the determination of the metal amounts that are bound within soil solid phases and knowledge the

chemical mechanism of metal binding are important for predicting possible metal transfer to the aquatic systems.

The total metal content in soil is partitioned between the solid phases, *i.e.*, phyllosilicate minerals, carbonates, sulfides, Fe, Al and Mn oxyhydroxides and organic matter.[1] In addition, the different mechanisms of binding of metal ions to the different phases (ion exchange, outer- and inner-sphere surface complexation (adsorption), precipitation or co-precipitation) influence their mobility and bio-availability to a great extent.[2] In order to determine the manner in which the total metal content is subdivided between the soil phases, fractionation of the metal content, either by ion exchange processes or by dissolution of selected soil phase, is required. For this purpose, a sequential extraction (SE) procedure was introduced and widely accepted, and subsequently, numerous extraction schemes, *i.e.*, according to Tessier, The European Community Bureau of Reference (BCR), Gibbs, Ure, Campanella, *etc.*,[3] in which different extraction agents and conditions were suggested, were adopted. Many studies have been conducted in an attempt to define the optimal extraction conditions and to harmonize operational extraction procedure, since the results obtained by application of different extraction schemes are often non-comparable. In addition, SEs often give unreliable results because of the non-selectivity of the extraction agents simultaneously for the selected phase and ions, precipitation of new mineral phases or redistribution of ions between already existing soil phases during extraction.[4] However, a major disadvantage of the SEs is related to the fact that they are time and labor consuming, and according to the Tessier or BCR scheme require an overall operation time of about 18 and 51 h, respectively. Thus, there exists considerable interest in the development of ultrasound-assisted extractions (UAE) or microwave-assisted extractions, which provide the same information as conventional SEs, but are faster to realize.

Initially, ultrasonic energy was used for the dispersion of soil aggregates[5] or the disintegration of sewage sludge,[6] since the ultrasonic cavitation phenomenon together with the turbulent flow of aqueous suspension of soil and acoustic streaming result in friction, stress and dispersion of soil aggregates. In addition, ultrasonic energy has been widely used for accelerating the extraction of metal,[7] aliphatic and polycyclic aromatic hydrocarbons[8] and organochlorine pesticides[9] from soil or other solid samples. Thereby, the ultrasonic energy was applied by the use of an ultrasonic probe,[10] an ultrasonic bath[11] or cup-horn sonoreactors[12] with the conclusion that the probe provides shorter extraction time (up to 100 times), while the ultrasonic bath enables simultaneous replicate extractions. Perez-Cid *et al.*[13] described an ultrasound-assisted BCR SE of Cu, Cr, Ni, Pb and Zn ions from sewage sludge, whereby the duration was only 22 min, while recoveries were similar to those obtained by the conventional BCR extraction. A similar study was conducted by Davidson and Delevoye[14] and as they reported, the

recoveries were similar to those of conventional shaking for all metals (Cu, Mn and Zn) except from the important matrix element Fe. Väisänen and Kiljunen[15] performed a five-step ultrasound assisted SE of As, Cd, Cu, Pb and Zn ions from soil sample, according to the Tessier scheme. With the exception of the As concentrations, which were too high, the results of the UAE procedure were highly comparable with the results obtained by the conventional procedure. Arain *et al.*[16] showed that by the use of optimized sonication conditions, a three-step BCR UAE could be successfully completed in 15–30 min, thus providing considerable time saving, with a high treatment rate and low sample and reagent usage. The acceleration of the first step of the BCR extraction for trace and matrix elements was investigated by Rusnák *et al.*,[17] whereby the experiment included soil, sediment and gravitation dust samples. The results showed that the effect of ultrasound was different for all the studied sample types and each element. According to Filgueiras *et al.*,[18] the ultrasound-assisted versions of the BCR extraction scheme showed a better performance than the Tessier ones in terms of obtaining good agreement with the conventional SE, with the best results being found for metal partitioning in sewage sludge. To summarize, according to some studies, UAEs have proved to be successful for achieving quantitative recoveries from various environmental matrices, such as soil, sewage sludge, marine and lake sediments and reference materials.[19] However, according to others, ultrasonic energy did not affect all the types of solid samples in precisely the same way as conventional shaking. When it comes to soil sample, the difficulty of developing a rapid version of SEs is related to the different fractionation patterns obtained by UAE in comparison to conventional ones, mainly for the matrix elements, such as Fe.[4]

The aim of this study was to investigate the influence of ultrasonic energy on aqueous suspensions of soil, through changes in different physico-chemical parameters, in order to determine whether ultrasound could be used for accelerating the extraction of major and trace elemental from soil samples.

A sample of serpentinite soil type Ranker was used as the substrate in this research. Rotary mixer-assisted extraction (RAE) and UAE were performed as single extractions using deionized water as the only extracting agent. A SE was performed in order to assess the amounts of heavy metals associated with different soil phases. For the determination of the cation concentrations in the soil extracts obtained by RAE, UAE and SE, inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements were performed. For all the soil suspension during the UAEs, conductivity (κ) measurements were continuously performed. Additionally, the UAEs were repeated in order to measure the suspension parameters, *i.e.*, the oxido-reduction potential (*ORP*), the particle size diameter (*PSD*), the zeta potential of the colloidal particles (*ZP*) and the pH, during the ultrasonic treatment.

EXPERIMENTAL

The soil sample was taken from a site covered with natural vegetation, at the location Bubanj Potok, near Belgrade, Serbia, which had been exposed to minimal influences of anthropogenic pollution. The geographical coordinates of the location are 44° 44' 4" North, 20° 32' 36" East and the height is 157 m above sea level. The soil sample, weighing 1 kg in total, was obtained by combining samples taken from the surface horizon, rich in humus, from 30 different sites, at a depth of 20 cm. The depth of the total soil profile at this location is 50 cm. The sample was air dried for 72 h. Subsequently, the large fractions were removed, crushed in a mortar and sieved through a 1 mm pore diameter sieve. The basic pedological analysis included: the potentiometric determination of the pH in H_2O and 1.0 mol L^{-1} KCl, the humus content after the Turin method, the adsorptive complex of the soil (H, T, S) after Kappen, determination of the soil texture by the pipette method, determination of the hygroscopic moisture by drying at 105 °C and determination of the mass loss during heating at 700 °C for 30 min.

The extraction suspensions were prepared in 50 mL volumetric flasks by mixing the soil sample with deionized water in a ratio 1:10, *i.e.*, 2 g:20 mL. Two series of three extractions each were performed using an Overhead Mixer Reax 20/8 (Carl Roth, Germany) rotary mixer in which the suspension was processed for 22 h mixing at 10 rpm at room temperature (20 °C). The second technique involved the use of an ultrasonic bath with the suspension positioned at the same place in the bath and at the same initial water temperature, 17 °C. Two extractions were made for each of the following extraction times: 10, 20, 30, 40 and 50 min. A Transsonic T 760 DH (Elma, Germany) ultrasonic bath operated at an ultrasonic frequency of 40 kHz and effective ultrasound power of 170 W was employed for these experiments. Deionized water (18.2 MΩ cm) produced by a Milli-Q Reagent Grade system (Phenomenex, USA) was used for the extractions and preparation of all suspensions. The substances used for the analyses were of high analytical purity. After the extraction processes were completed, each of the extraction suspensions was first centrifuged, then filtered through medium pore size filter paper and finally through 0.2 μm pore size syringe membrane filter (Phenomenex, USA). The thus obtained soil extract was acidified by addition of 1 μl of 70 % concentrated perchloric acid (Merck, Germany) per 1 mL of extract and preserved at 4 °C in a laboratory refrigerator for further analysis.

Furthermore, the soil sample was subjected to SE according the scheme suggested by the Standards, Measurements and Testing Program of the European Commission (BCR, formerly).[3] The last step of the extraction procedure using *aqua regia*, according to EPA 3050B digest extract method was added in order to determine the total metal contents. Additionally, in order to distinguish between the easily reducible fraction bound to Mn oxyhydroxides and the moderately and poorly reducible one bound to amorphous and crystalline Fe and Al oxyhydroxides, the procedure was modified by the inclusion of a third extraction step.[20] Dry soil samples (1 g) were weighed into 50 mL polystyrene flasks and after addition of the extraction agents, the flasks were shaken on a rotary mixer at 15 rpm. The residue was washed with 25 mL of deionized water, and centrifuged at 3000 rpm, prior to the next extraction step. The extraction was performed in triplicate, according to the procedure summary (Table I).

A Thermo Scientific iCAP-6500 DUO ICP (Thermo Fisher Scientific, UK) spectrometer, with continuous wavelength coverage ranging from 166 to 847 nm, equipped with RACID86 charge injector device (CID) detector, pneumatic cross-flow type nebulizer and quartz torch, was used for the ICP-OES measurements. The instrumental conditions were set at: input power, 1150 W; auxiliary gas flow, 0.5 L min^{-1}; coolant gas flow, 12 L min^{-1} and nebulizer

flow, 0.7 L min^{-1}. For ICP-OES calibration, multi-element plasma standard solution 4, Spec-pure (Alfa Aesar, Germany, Cat. No. 42885) was used and two series of standard solutions were prepared: for alkali and alkaline earth metal elements of concentration 0.01, 0.05, 1, 10 and 50 mg L^{-1} and for the transition elements of concentration 0.1, 1, 10, 100 and 500 µg L^{-1}. The relative standard deviation was calculated automatically, $RSD = (SD/\mu)\times100$, where SD is standard deviation and μ represents the mean value of three measurements. After accuracy evaluation, the relative standard deviations of the ICP-OES measurements were determined to be: Al, 1.06 %; Ca, 0.21 %, Cd, 8.69 %; Co, 6.91 %; Cr, 7.17 %; Cu, 6.21 %; Fe, 0.63 %; K, 2.68 %; Mg, 0.79 %; Mn, 4.86 %; Na, 0.82 %; Ni, 8.42 %; Pb, 7.62 % and Zn, 8.67 %.

TABLE I. A summary of the SE operating conditions

Elements fraction	Extraction time, h	Agitation method	Extractant amount, mL	Extraction reagent
Water-exchangeable, weakly adsorbed	16	Shaking, room temp.	40	0.11 mol L^{-1} acetic acid (HOAc)
Easily reducible (Mn oxyhydroxide phase bound)	16	Shaking, room temp.	40	0.1 mol L^{-1} NH$_2$OH·HCl/HNO$_3$ pH 2
Moderately reducible (Fe, Al oxyhydroxide phase bound)	10	Shaking, room temp.	40	0.2 mol L^{-1} ammonium oxalate/ 0.2 mol L^{-1} oxalic acid
Oxidizable (organically bound)	3	Occasional agitation, 85 °C	2x10	30 % (8.8 mol L^{-1}) H$_2$O$_2$/HNO$_3$ pH 2
	16	Shaking, room temp.	40	1 mol L^{-1} NH$_4$OAc, pH 5
Residual	0.5	Water bath, 95 °C	10	*Aqua regia*, HNO$_3$/HCl (1:3)

With the exception of κ, for the determination of each suspension parameter, additional UAEs were performed in five replicates with an aqueous soil suspension. In order to adjust ionic strength for the κ measurement, the extraction solutions were prepared with an ionic strength buffer (1 mol L^{-1} KCl) instead of deionized water. The conductivity, *ORP* and pH measurements were performed using a 3540 Conductivity/pH meter (Jenway, UK). The *PSD* and *ZP* measurements were performed by dynamic light scattering spectroscopy using a Zeta-sizer Nano Red ZS, with a 633 nm He–Ne laser (Malvern, UK). The instrumental conditions were set at: run duration, 10 s; temperature, 25 °C; refractive index of material, 1.600 and absorption index, 0.01. The measurements were conducted during the extraction process every 10 min for the colloid *PSD* and *ZP*, every 5 min for *ORP* and pH, while the value of κ was measured continuously. For the duration of the pH and *ORP* measurements, the ultrasonic bath was turned off.

RESULTS AND DISCUSSION

The measured pH value in 1 mol L^{-1} KCl was 6.0 and in deionized water, the pH value was (5 g soil:10 mL water) 6.9. The results of the other pedological analyses are given in Table II.

TABLE II. The results of the basic pedological analysis

Soil parameter	No. 1	No. 2	No. 3	Mean value
Humus, %	5.15	5.23	5.12	5.16
Total C, %	2.99	3.03	2.97	2.99
The sum of base cations, mEq 100 g^{-1}	34.6	33.5	39.6	35.9
Large sand particles, %	4.87	6.22	6.83	5.97
Small sand particles, %	30.10	30.8	31.58	30.85
Colloid clay, %	45.75	43.61	40.99	43.45
Silt, %	19.28	19.28	20.60	19.72
Hygroscopic moisture, %	3.1	3.1	3.1	3.1
Heating loss, %	14.2	14.6	14.4	14.4

According to the results, the investigated soil sample contained low levels of some elements; thus, the extracted amounts of Li were in range from 0.003 to 0.024 mg 100 g^{-1} soil, the extracted amounts of Cd were in the range of 0.386 to 0.963 µg 100 g^{-1} soil and for Co the values ranged from 0.101 to 0.969 µg 100 g^{-1} soil. Since the amounts of these elements extracted by both extraction techniques were too small for conclusions to be drawn, these elements were not taken into further consideration.

A comparison of the amounts of the elements extracted by UAE and RAE is shown in Fig. 1, from which it can be seen that significantly higher amounts of the matrix elements (Fe, Al and Mn) were extracted in the UAE than in the RAE. Compared to the amounts extracted using the rotary mixer, the average amounts of Fe and Al ions extracted during the UAE were 7.5 and 8.2 times higher, respectively. However, in the case of the alkaline earth elements (Ca and Mg), higher amounts were extracted in the RAE than in the UAE. Considering the concentrations of Mg ion, the high amounts extracted using both techniques could be explained by the properties of the soil itself, since Ranker over serpentinite type of soil has a ratio Ca:Mg<1, unlike other soil types.[21] The lower amounts of the alkaline earth elements were obtained using UAE compared to those extracted by RAE could be explained either by the significantly longer agitation time of the RAE (22 h) and subsequent dissolution, or by the re-adsorption of extracted cations onto the sorption sites newly exposed by the influence of ultrasound.

The amounts of all elements extracted in the UAE as a function of sonication time are shown in Fig. 2, from which it can be seen that the extracted amounts of all elements changed, which was most noticeable in the case of the matrix elements (Fe, Al and Mn) and some trace elements (Cr, Cu and Zn).

During the UAE, the pH also changed in the range of 5.60 to 8.12 (Fig. 3). As it can be seen in Fig. 3, the largest increase in pH to 8.12 was registered after 20 min of sonication, at the same time a decrease of the acid (Al and Fe) and the increase of the base cation (Mg and Ca) concentrations were observed in the extract. At an extraction time of 40 min, the extracted amounts of both base and

acid cations were the largest observed, but the pH fell simultaneously to 7.58, indicating that the total content of acid cations (Al, Fe and Mn) exceeded the total content of base cations (Ca and Mg). With further increase in the sonication time, the extracted amounts of Fe, Al and Mn decreased and a subsequent increase in the pH of the soil suspension was observed. It is assumed that the changes in the pH value were caused by adsorption and desorption processes, but were not the cause of these processes. Large amounts of various cations were released into the solution, influencing the pH change. This pH change can influence the adsorption and desorption processes to some extent, but these processes are mainly related to competitive cation interactions for the sorbing phase and the exchange of sorbed cations with those from solution is influenced by ultrasound.
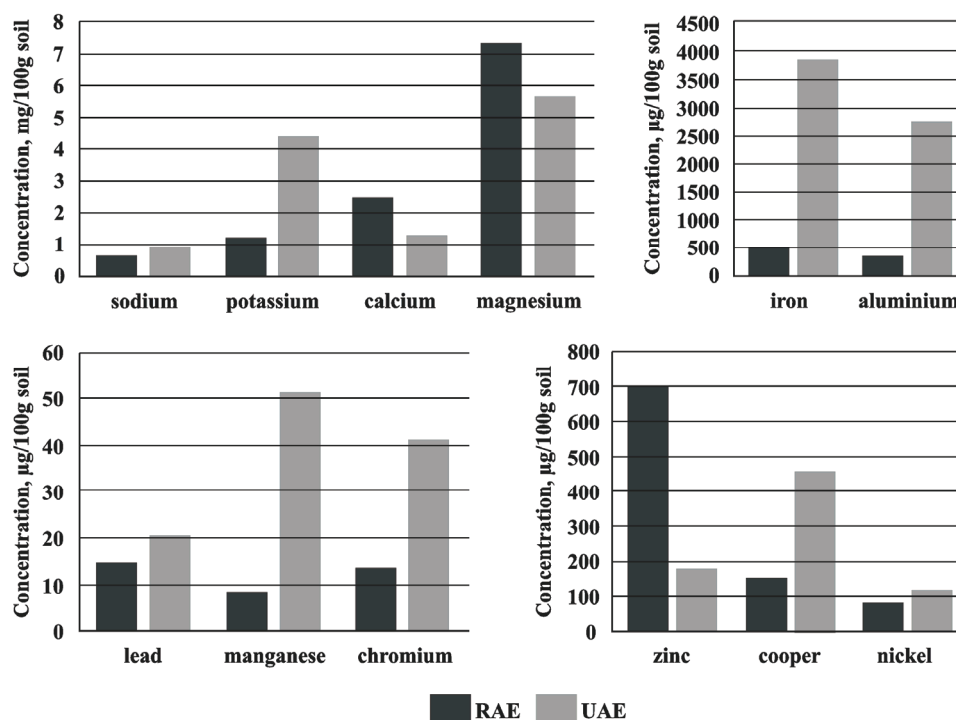

Fig. 1. Comparison of the average amounts extracted using a rotary mixer and ultrasound.

The results of the SE procedure, obtained for Cd, Co, Cr, Cu, Ni, Pb, Zn, Fe, Al and Mn, are shown in Table III. Considering that deionized water was used as the extraction agent in the UAE and RAE processes, the extracted amounts are significantly lower compared to the amounts extracted by means of the chemical agents proposed in the SE procedure. Thus, the results present the percentage of the total content of elements contained in the water-exchangeable, easily and

moderately reducible, oxidizable and residual fraction. Although not the most abundant in the soil, the oxyhydroxides of Fe, Al and Mn have a large surface area, which makes them important reactive phases with respect to metal sorption. Concerning the other fractions, the largest amounts of Cr and Cu ions were contained within the moderately reducible fraction and hence associated with the amorphous and crystalline Fe, Al oxyhydroxides.
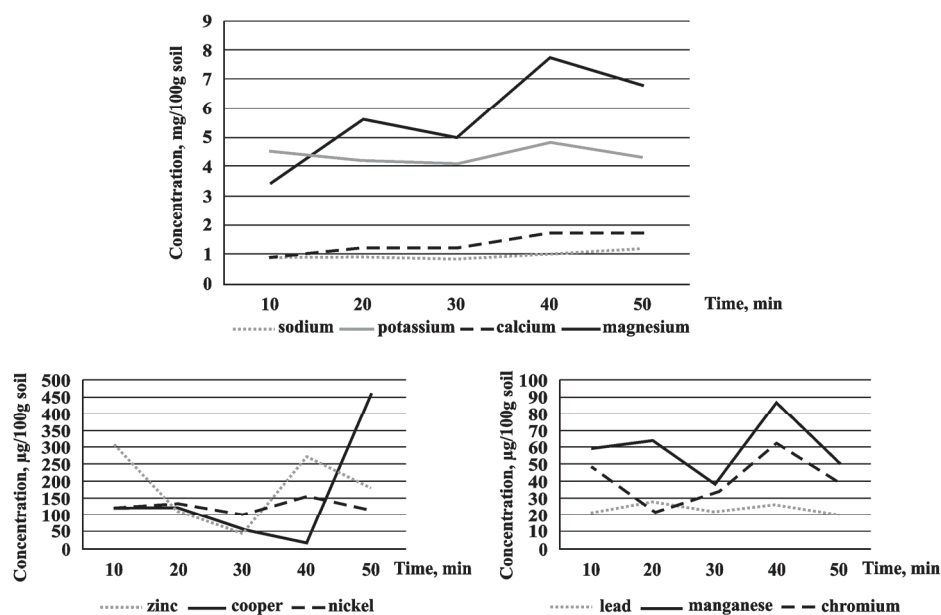

Fig. 2. The effectiveness of the UAE for the extraction of Na, K, Ca, Mg, Pb, Mn, Cr, Zn, Cu and Ni ions as a function of sonication time.
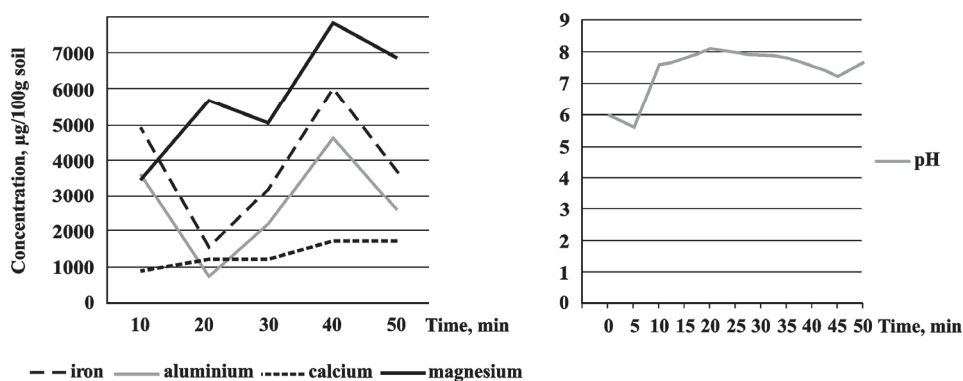

Fig. 3. The effectiveness of the UAE for the extraction of Fe and Al ions (left) and changes in pH value (right) as a function of sonication time.

Furthermore, the largest amounts of Cd, Co, Ni, Pb and Zn ions were contained within the easily reducible fraction of elements, which are associated with Mn oxyhydroxides. The manner in which metals are retained in the soil refers to the type of surface sorption complex, which is influenced by surface loading, as well as by pH, ionic strength and type of sorbing phase. Hence, outer-sphere complexation is a rapid and reversible process that involves electrostatic interactions and occurs on surfaces of opposite charge. On the contrary, inner-sphere complexation can increase or reduce the surface sorptive charge regardless of the original charge.[22] Since sorption includes adsorption, precipitation and polymerization, the sorption mechanisms can be determined only through molecular investigations by use of spectroscopic techniques.

TABLE III. The results obtained by the SE procedure. Participations of different metal fractions in total metal content, %. Bold values present the largest non-residual fraction for each element

Fraction	Cd	Co	Cr	Cu	Ni	Pb	Zn	Fe	Al	Mn
Water-exchangeable	–	0.05	–	–	1.4	0.01	–	–	–	1.4
Easily reducible (Mn oxyhydroxides)	**90.3**	**49.9**	0.9	1.2	**17.1**	**18.9**	**15.4**	1.2	1.6	**73.5**
Moderately reducible (Fe and Al oxyhydroxides)	9.7	14.7	**17.8**	**22.7**	7.1	1.3	6.5	**13.2**	**6.2**	10.3
Oxidizable	–	3.9	16.3	0.05	15.8	5.9	5.1	0.1	0.3	1.6
Residual	–	31.5	65.0	76.0	58.6	73.9	72.9	85.5	92.0	13.2

The changes in extracted amounts of some trace elements (Cr, Cu and Zn) as a function of sonication time are dependant on the cation sorption mechanism, as well as on the type of mineral or organic matter with which they are associated. According to Charlet and Manceau,[23] Cr (III) can be found on goethite (iron oxyhydroxide) surfaces, either adsorbed as an inner-sphere complex or in the form of Cr hydroxide surface precipitates. The results of the SE showed that 17.8 % of the total Cr content (50.8 % of the non-residual content) was associated with Fe and Al oxyhydroxides. In keeping with this, as shown in Figs. 2 and 3, the increases in the extracted amounts of Fe and Cr with the extraction time follow the same change pattern. The same pattern of change was observed in the case of Mn and Zn. Scheinost et al.[24] demonstrated that Zn(II) can form both inner-sphere surface complexes and a Zn hydrotalcite-hydroxide phase upon sorption to Al-bearing minerals, inner-sphere surface complexes on goethite and both inner-sphere and multinuclear hydroxo-complexes on manganite surfaces. In the studied soil sample, Zn had predominantly formed complexes on manganite surfaces since, according to the SE results, 70.3 % of the non-residual content of Zn was associated with Mn oxyhydroxides within the easily reducible fraction. According to Weesner and Bleam,[25] Cu(II) can form outer- and inner-sphere surface complexes upon sorption to boehmite (Al oxyhydroxide). This observation was

confirmed by the results of the SE, which showed that 94.8 % of non-residual content of Cu was found within the moderately reducible fraction. However, the variations in the changes of pattern of the extracted amounts of Cu and Al were not the same, which implies that certain portions of the metal released by ultrasonic treatment were re-adsorbed onto the other remaining soil phases.

An explanation could be suggested for the high amounts of extracted matrix elements (Fe, Al and Mn), as well as to the variations of the amounts of extracted cations with increasing sonication time. First, the influence of the ultrasound on the aqueous soil solution could be attributed to the cavitation effect. The cavitation is caused by interaction of the ultrasound with soil solution, by implosion of cavitation bubbles, subsequent increases in the local pressure and the formation of elastic shock waves. This leads to the production of localized high temperatures in the solution and thus creates extreme conditions for chemical reactions to occur. At the beginning of the ultrasonic extraction, the temperature of the water was 17 °C and the increase in temperature was 11 degrees, which makes 28 °C at the end of the extraction process. This rise in the temperature influences on the amounts extracted, however it is hard to measure to what extent. The maximum temperature T_{max} and maximum pressure P_{max} in the cavitation bubble before collapse is defined as:

$$T_{max} = T_{in} \left[P_a (\gamma - 1)/P_{in} \right] \tag{1}$$

$$P_{max} = P_{in} \left[P_a (\gamma - 1)/P_{in} \right]^{\gamma/(\gamma - 1)} \tag{2}$$

where T_{in} and P_{in} are the initial temperature and pressure in the bubbles, respectively, P_a is the acoustic pressure at the beginning of collapse and γ is the average specific heat ratio at constant volume of the gas in the bubble.[26] Furthermore, the temperature and pressure rise inside cavitation bubbles leads to the formation of free radicals. Related to this, the application of ultrasound for decomposition of different organic contaminants in water has been widely researched. In these reactions, the production of highly reactive oxygen species by sonolysis of water molecules, *i.e.*, hydroxyl-, peroxy- and superoxide- radicals, is considered to play an important role. Their generation is supposed to occur on the inside/interface of the adiabatic cavitation bubbles that are formed in aqueous suspensions during sonication.[27] In the present case, the effectiveness of the sonochemical decomposition of water was also highly dependent on the presence of soil particles, which could facilitate the cavity formation process and thereby intensify the generation of radical species. According to Tuziuti *et al.*,[28] the presence of soil particles can also influence the scattering of the ultrasound waves followed by subsequent attenuation of the cavitation effect and decrease in formation of reactive species. Once generated, highly reactive species influence changes in the redox status in the soil suspension. The changes in the redox status have a large influence on the mobility of certain metal species, such as Fe, Mn

and Cr. Under reductive conditions, oxyhydroxides of Fe and Mn are subjected to reductive dissolution and hence metal species, associated with these phases can have changes in solubility. Related to this, the conducted measurements showed that the *ORP* of the extraction suspension increased within 5 min after stopping sonication from 30 to 130 mV *vs.* Ag/AgCl, 3 mol L^{-1} KCl reference electrode, probably due to the generation of multiple redox couples.

In addition to this, ultrasound has an influence on desorption processes and the ability of ultrasonic energy to intensify desorption processes and to release metals from soil, activated carbon or other materials with high sorption capacity is well documented. Hwang *et al.*[29] showed that the efficiency of leaching solutions (both citrate and EDTA) for heavy metal removal from soil was increased with sonication compared to those of soil washing. Hamdaoui *et al.*[30] explored the effects of ultrasound on the desorption of metal ions from activated carbon, and the results of the conducted study indicated that the desorption rates of Cu(II), Mn(II), Hg(II) and Cr(VI) were significantly improved by ultrasonic irradiation.

Beside desorption, re-adsorption processes are also intensified under the influence of ultrasound. The re-adsorption process and subsequent decrease of the extracted amount after 40 min of sonication occurred in the cases of all other mentioned elements, also of Fe, Al, Mn, Cr and Zn. The rate of adsorption and re-adsorption in soils is dependent on the type and quantity of inorganic and organic components and the charge and radius of the ion being considered.[31] Surface reactive sites of the soil phases comprise permanent and variable charge sites, depending on their origin. For example, various functional groups, such as phenolic, carboxyl and alcoholic, are found on organic molecules. The major inorganic surface functional groups are the siloxane, associated with the silica tetrahedral layer of phyllosilicates and hydroxyl groups, such as silanol and aluminol, originating from broken mineral lattice of clay minerals or associated with the edges of metal oxyhydroxides. However, besides the mentioned reactive groups, ultrasonic energy can cause fragmentation of the soil particle and dispersion of soil aggregate, thus increasing the surface area available for reaction with the extraction agent. Sonication produces a significant increase of the specific surface area due to particle size reduction; hence, the number of sites available for adsorption is increased. Factors affecting soil aggregate dispersion during ultrasound application are the soil–water ratio, the total applied energy and the power output per volume of the extracting suspension. This was explained by enhanced surface diffusivity, which is related to the phenomena induced by acoustic cavitation, such as acoustic vortex micro-streaming, high-speed microjets, high-pressure shock waves and intense localized heating. In the aqueous soil suspension, ultrasonic treatment modifies the particle size, morphology and structural order of clay minerals. The elongated crystals are broken up into smaller units

that retain the typical lamellar morphology of the starting crystals.[32] The results of *PSD* analysis of the sonicated suspensions are given in Table IV, from which it could be seen that the mean particle size decreased with increasing sonication time.

Thereby, the *ZP* of colloid particles ranged from –49.54 to –11.08 mV with the largest change being observed between 40 and 50 min of sonication. *ZP* values more negative than –30 mV are considered to represent sufficient mutual repulsion to ensure the stability of a suspension.[33] It could be assumed that due to Fe, Al and Mn sorption processes in the last 10 min of sonication, the surface charge of colloidal particles decreased, and simultaneously the *PSD* showed a slight increase. As the results showed (Table IV), the suspension κ increased during sonication, partly due to the heating of the suspension and partly due to an increase in the number of total charged particles in the suspension.

TABLE IV. Changes in the colloid *PSD*, *ZP* and conductivity of extraction suspension as a function of sonication time

Extraction time, min	Detected particle size fraction, nm	Fraction participation, %	Average particle size, nm	Zeta potential mV	Conductivity μS cm^{-1}
10	4843	14.2	1258	–25.42	18
	1127	39.8			
	265	46.0			
20	4853	12.7	1090	–35.82	20
	860	47.8			
	158	39.5			
30	4886	10.2	1074	–28.04	23
	690	81.4			
	163	8.4			
40	4294	9.3	966	–49.54	28
	653	85.7			
	141	5.0			
50	4731	7.7	970	–11.08	38
	691	86.3			
	156	6.0			

CONCLUSIONS

As indicated above, the influence of ultrasonic energy on the soil sample preparation was found to be significant. However, not only due to a possible decrease in the extraction time, but mainly due to the expressed selectivity for the matrix elements (Fe, Al and Mn) and heavy metal portions associated with Fe, Al and Mn oxyhydroxides. As shown, the interaction of ultrasonic energy with the aqueous soil suspensions, alternately, influenced the processes of cation adsorption and desorption, thereby leading to a change in the extracted amounts of cations as function of sonication time. In addition to the aforementioned, the interaction of ultrasonic energy with the soil suspension created extreme conditions for chemical reactions to occur, some of them resulting in the generation of

highly reactive species. Therefore, it could be concluded that ultrasound cannot simply replace conventional treatments, such as conductive heating, in each extraction step of the sequential procedure. The introduction of ultrasound requires further investigation, first, to determine whether it has the same effect on different soil samples. Further investigations are required in order to explore whether ultrasound can be used to assess the heavy metal fraction associated with the easily reducible Mn oxyhydroxides and moderately reducible Fe and Al oxyhydroxides. For this purpose, ultrasound could be combined with deionized water only in particular SE steps for the efficient enhancement of the SEs, since compared to salt and acid solutions, deionized water is a preferable extractant, leading to avoidance of sample contamination.

И З В О Д

ЕКСТРАКЦИЈА ГЛАВНИХ ЕЛЕМЕНАТА И ФРАКЦИЈЕ ТЕШКИХ МЕТАЛА ВЕЗАНИХ У СКЛОПУ Fe, Al И Mn ОКСИДНИХ ФАЗА ЗЕМЉИШТА ПОТПОМОГНУТА УЛТРАЗВУКОМ

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Вршена је екстракција главних катјона и катјона елемената у траговима из узорка земљишта помоћу дејонизоване воде употребом ротационе мућкалице и ултразвучне каде са екстракционим временом од 10, 20, 30, 40 и 50 min. Узорак земљишта је подвргнут секвенционалној екстракцији према BCR процедури. Садржај добијених екстракта земљишта је одређен оптичке емисионе спектрометрије са индуктивно спрегнутом плазмом, и према резултатима екстракција изведена помоћу ротационе мућкалице се показала ефикасном у случају земноалкалних елемената. Употребом ултразвука екстраховане су неколико пута веће количине матрикс елемената (Fe, Al и Mn) и тешких метала који се у земљишту претежно налазе у склопу Fe, Al и Mn оксидне фазе. Продужење екстракционог времена није резултирало повећањем екстраховане количине. Током ултразвучне екстракције вршена су мерења проводљивости, pH, оксидоредукционог потенцијала суспензије земљишта, величине и зета потенцијала колоидних честица. Предложено је објашњење механизма екстракције и утицаја ултразвука на екстракцију главних елемената и тешких метала из оксидних фаза земљишта.

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