

## Extractability of sodium ions from soil

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**Abstract:** In this study, soil samples from two selected locations: "A" (alluvial soil) and "B" (clay loam) were analyzed. Chemical analysis of soil samples included determination of soil pH and soil suspension conductivity. Two different extraction methods were applied: shaking and ultrasound method for extraction of sodium ions from soil with three solvents (aqua regia, 5% CH<sub>3</sub>COOH and distilled water). The values of pseudo-total (extracted with aqua regia) and bioavailable Na content (extracted with 5% CH<sub>3</sub>COOH and distilled water) in the soil sample "A" were in the range of 46.35-66.55 mg Na/kg; 14.77-18.59 mg Na/kg and 12.58-15.20 mg Na/kg of soil, respectively, by applying shaking method. By the same method, in the case of soil sample "B" the ranges were 17.15-75.66 mg Na/kg; 20.87-32.80 mg Na/kg and 4.62-20.33 mg Na/kg of soil, for the extraction by aqua regia, 5% CH<sub>3</sub>COOH and distilled water, respectively. Ultrasonic extraction in all cases gained higher results compared to the shaking method. In general, the application of ultrasound shows a positive effect on the extractability of Na<sup>+</sup> ions from soil samples.

## INTRODUCTION

Sodium is found in the soil and plants as monovalent and belongs to the group of nutrients (Lutgens and Tarbuck, 2003). It has the role of electrolyte, due to its high content in the protoplasm, it affects its hydration - it is important in the regulation of water content. The availability of metals to plants, as well as the migration of metals to deeper soil layers, largely depends on the fractions in which the metals are found in the soil. The metal fractions in the soil are exchangeable ions, carbonates, Fe and Mn oxides, organic and residual fractions (Liang, Wang, Gao et al., 2014, Slukovskaya, Kremenetskaya, Drogobuzhskaya et al., 2020). The distribution of metals between different forms in which they can be found in the soil is controlled by both physical and chemical processes and time intervals (Acosta, Jansen, Kalbitz et al., 2011). Therefore, it is possible that individual metals in the soil occur in several different

chemical forms depending on the type of metal and physicochemical properties of soil (Tessier, Campbell, Bisson et al., 1979; Kotoky, Bora, Baruah et al., 2003; Du, Xue, Liu et al., 2008; Cui and Du, 2011). The decomposition of the soil primary minerals of Feldspar releases sodium, which for the most part immediately binds to the adsorption complex of the soil. This reduces the mobility and risk of leaching from the soil, except in sandy soils. If the adsorption complex contains more than 15% Na<sup>+</sup> ions, the soil is classified as alkaline soils (multivalent cations are most strongly bound to the adsorption complex, with the exception of H<sup>+</sup> ion, due to its smaller diameter it has a higher binding strength). Cations of lower retention (retention power on the adsorption complex) are the easiest to desorb, and Na<sup>+</sup> ion has the weakest retention, primarily due to the large hydration membrane. When NaCl content in the soil exceeds 0.5%, the problem of salinity occurs (Kamber and Unlu, 2010). Salinity, in the form of NaCl, is one of

the main abiotic stresses that reduces plant growth and development (Maathuis, Ahmad and Patistan et al., 2014). Some metals can bind more strongly to the solid phases of the soil, resulting in poorer desorption. Therefore, in metals that have a high affinity for binding to the solid phase, the efficiency of its removal is lower than in other metals. Today, salinity is one of the most important factors threatening the sustainability of irrigated agriculture. Salinity reduces the productivity if not brought under control (Kanber and Unlu 2010). Furthermore, excessive amounts of sodium ruin the physical structure of the soil. The root development is also affected due to the aggregate's fragmentation causing a decline in water and air permeability (Karadağ, Eren, Çetinkaya et al., 2015). For the experimental part of this work, two different soil samples were taken from the surface layer (up to 20 cm depth) marked as: soil "A" (alluvial soil) and soil "B" (clay loam). The bioavailable sodium content of the soil was determined by extraction with selected green solvents (H<sub>2</sub>O and 5% CH<sub>3</sub>COOH) using two methods of extraction: ultrasound and shaking. The obtained results were compared with the pseudo-total content of sodium in each soil, which was determined according to BAS ISO 11466: 1995 (E). Sodium content was determined by atomic emission spectrometry. The obtained results enabled the evaluation of the efficiency of the applied extraction methods.

## EXPERIMENTAL

### *Reagents and solutions*

All used reagents were of analytical grade. CaCl<sub>2</sub>·2H<sub>2</sub>O, p.a., HCl, 36% p.a., HNO<sub>3</sub>, 65% p.a., and CH<sub>3</sub>COOH, 96% p.a. were obtained by Semikem, Sarajevo. Standard Na solution (Certi PUR 1000 mg/L), and KNO<sub>3</sub>, 2000 mg/L were obtained by Merck, Darmstadt. Working solutions were prepared by diluting Na standard solution.

### *Analysis*

The analysis included the following experimental steps: sampling of two different soil samples (marked as soil "A" and soil "B") and dividing them into 10 subsamples with two parallels (A1-A10 and B1-B10); determination of the moisture content (%) in soil samples; preparation of soil suspension in water and in CaCl<sub>2</sub>·2H<sub>2</sub>O to determine pH and conductivity. Sodium extraction from the soil samples referred as pseudo-total sodium content was performed by the method BAS ISO 11466:1995 (E). Furthermore, sodium extraction from the soil samples was tested by the extraction of soils in distilled water and 5% acetic acid by ultrasound and shaking to determine the effectiveness of the tested methods and solvents.

### *Soil type, sampling and preparation of soil samples*

Soil samples analyzed for sodium content were sampled from two locations in Bosnia and Herzegovina and marked as: soil sample A and soil sample B. The soil sample A belongs to the type of alluvial soil, due to the river nearby, while soil itself belongs to the category of clayey sand. The soil was fertilized with burnt manure,

while the crops in the previous vegetation were: real grains (barley, wheat, oats and spelled), and vegetables (tomato, watermelon, parsnips and peas). The soil sample B belongs to the type of clay loam. The classification of analyzed soils was performed by the Institute for pedology, agrochemistry and melioration, Sarajevo, Bosnia and Herzegovina. For fertilization of this type of soil in the previous vegetation, beef manure was used, while the crops in the previous vegetation were: potatoes (which were additionally fertilized with artificial fertilizer NPK formulation 15:15:15) and tomatoes (which are additionally fertilized with sheep manure and artificial fertilizer NPK with a formulation of 7:20:30).

From both locations, 10 kg of each soil samples were taken from the surface layer of the soil (depth up to 20 cm), with a plastic spatula from the arable layer. The samples were cleaned of pieces of organic origin and stones, air-dried and stored in 2 L polyethylene bags. Afterwards, air-dry soil samples were ground in a porcelain mortar and sieved through a 2 mm sieve to eliminate all impurities. To minimize the humidity impact on the method, precision samples were dried at 105°C to the constant weight.

### *Determination of active soil reaction, substitution acidity and electrical conductivity*

Determination of active (pH in water) and substitution acidity (pH in calcium chloride dihydrate solution) in soil samples (A and B) was performed according to the method of BAS ISO 10390:2006. The pH of the soil is potentiometrically determined from the soil-water suspension in a ratio of 1:5, giving information on the active acidity of the soil, while measuring the pH of the soil suspension in 0.01 mol/L CaCl<sub>2</sub>·2H<sub>2</sub>O solution indicates the value of the soil substitution acidity. For determining the specific conductivity of the soil which is a consequence of the presence of free ions, i.e. soluble salts in the soil, the same aqueous suspension of soil is taken as for determining the pH.

### *Determination of the pseudo-total amount of sodium in soil samples*

From the prepared soil samples, 20 parallels weighing 3 g (±0.1 mg) were transferred to balloons with a ground neck and a flat bottom of 250 mL. 21 mL of HCl and 7 mL of HNO<sub>3</sub> were added to the samples. Solvent soil samples were placed in a digester and digestion was performed for 16 hours at room temperature and then continued at 108°C for 2 hours. The samples were then cooled and filtered into a 100 mL volumetric flask over quantitative filter paper, marked with corresponding labels and filled to the mark with 0.5% HNO<sub>3</sub>. The resulting solutions were used to determine the pseudo-total Na content by atomic spectrometer Varian AA240FS in emission mode.

### *Determination of water-soluble and exchangeable soil fraction*

From the prepared soil samples, 20 parallels weighing 10 g (±0.1 mg) were transferred to polyethylene bottles with the corresponding label. 50 mL of distilled water was added to the samples to determine the water-soluble

forms of Na from the soil. Sample vials were placed in a shaker by shaking the samples at room temperature for 2 hours at 180 rpm. The samples were then filtered into a 100 mL volumetric flask over quantitative filter paper and diluted to the mark with distilled water. The obtained filtrates were immediately tested for Na content by the AES method. At the same time, 20 more parallels were prepared in the same manner, only by replacing distilled water with 5% CH<sub>3</sub>COOH acid in order to determine the exchangeable soil fraction. To suppress ionization, potassium nitrate solution with a potassium concentration of 2000 µg/mL was added to each sample as well as to each blank probe.

#### Ultrasonic extraction of sodium from a soil sample

From the prepared soil samples, 20 parallels weighing 3 g (±0.1 mg) were weighed. 21 mL of HCl and 7 mL of HNO<sub>3</sub> were then added to the weighed samples, according to the BAS ISO 11466:1995 (E). The samples were then placed in an ultrasonic bath with a frequency of 37 kHz, for 2 hours. The contents of the vessels were then filtered through filter paper (blue tape) into 100 mL volumetric vessels and filled up with distilled water. The obtained filtrates were used to determine Na content by AES-flame technique. Furthermore, 20 parallels weighing 10 g (±0.1 mg) and 3 g (±0.1 mg) were weighed in the same way to determine the effect of ultrasound on the efficiency of Na<sup>+</sup> ion extractability in the case when distilled water and 5% acetic acid were used as solvent, respectively. The samples were therefore poured with 50 mL of distilled water and 50 mL of 5% CH<sub>3</sub>COOH, respectively, and placed in an ultrasonic bath for 2 hours at 37 kHz. The contents of the vials were filtered through quantitative filter paper into 100 mL volumetric vessels and made up to the defined volume with distilled water. The obtained filtrates were used to determine the Na content by the AES method.

The calculation of the metal content in the soil was done according to the formula (Eq.1):

$$(\text{mg Na}) / (\text{kg soil}) = (c \cdot V \cdot f) / m \cdot 100 \quad \text{Eq. 1}$$

where:

c (mg/L) - metal concentration,

V (L) - solution volume;

m (g) - mass of air-dry soil sample;

f- dilution factor.

## RESULTS AND DISCUSSION

#### Moisture content of soil samples

The moisture content in a total of 20 analyzed samples was determined gravimetrically based on weight loss by drying the samples at a temperature of 105°C to constant weight. The obtained results are given in Table 1. The mean value of moisture content in the soil samples "A" is 15.34% and 12.41% for soil samples "B".

**Table 1:** Moisture content in soil samples (%)

Sample A	Sample B
A1=11.34 %	B1=11.95 %
A2=16.28 %	B2=12.67 %
A3=17.47 %	B3=12.98 %
A4=15.03 %	B4=10.17 %
A5=17.22 %	B5=10.24 %
A6=14.24 %	B6=14.17 %
A7=15.83 %	B7=11.65 %
A8=17.91 %	B8=12.98 %
A9=17.63 %	B9=13.11 %
A10=10.40 %	B10=14.13 %

#### Active and substitutional soil acidity and electrical conductivity of soil samples

pH is an important indicator of soil quality, plays a significant role in many soil processes such as solubility and availability of plant nutrients, microbial activity and degradation of organic matter in the soil, sorption of contaminants and various physicochemical processes involved in the biogeochemical cycle (Sintorini, Widyatmoko, Sinaga et al., 2021). The results of pH values determined in the suspensions of soil with water (active acidity) and with 0.01 mol/L CaCl<sub>2</sub>x2H<sub>2</sub>O (substitution acidity) for soil samples "A" and "B" were presented in Table 2, as well as the values of electrical conductivity in suspension with distilled water.

**Table 2:** The result of pH value and electrical conductivity of soil samples.

"A"				"B"			
Samples	pH (H <sub>2</sub> O)	pH CaCl <sub>2</sub> x 2H <sub>2</sub> O	Conductivity (µS/cm)	Samples	pH (H <sub>2</sub> O)	pH CaCl <sub>2</sub> x 2H <sub>2</sub> O	Conductivity (µS/cm)
A1	6.02	5.08	231	B1	6.71	6.10	1068
A2	6.11	5.11	263	B2	7.46	6.60	626
A3	6.13	5.34	270	B3	6.74	6.09	598
A4	7.61	6.86	492	B4	5.89	4.90	187
A5	6.29	5.33	300	B5	5.85	4.96	289
A6	6.85	6.14	617	B6	6.99	6.25	600
A7	6.06	6.03	452	B7	6.95	6.21	466
A8	6.76	6.02	362	B8	6.56	5.94	501
A9	7.00	6.25	333	B9	6.96	6.23	658
A10	6.15	5.63	323	B10	6.97	6.11	685
Min	6.02	5.08	231	Min	5.85	4.90	187
Max	7.61	6.86	617	Max	7.46	6.60	1068
*Avg.	6.50	5.78	364	*Avg.	6.71	5.94	568
**SD value	0.58	0.62	133	**SD value	0.55	0.60	275

\*Avg= Average value; \*\*SD value- standard deviation

The obtained average pH value (6.50; 6.71) of the analyzed soil samples determined in water from the soil samples “A” and “B”, respectively, shows that analyzed soils belong to the class of neutral and slightly acidic soils (Sirsat, Cernadas, Fernández-Delgado *et al.*, 2017). Nevertheless, the difference in the pH value of different soil samples from the same plot is also due to the inhomogeneous distribution of the fertilizer used to fertilize the investigated plot.

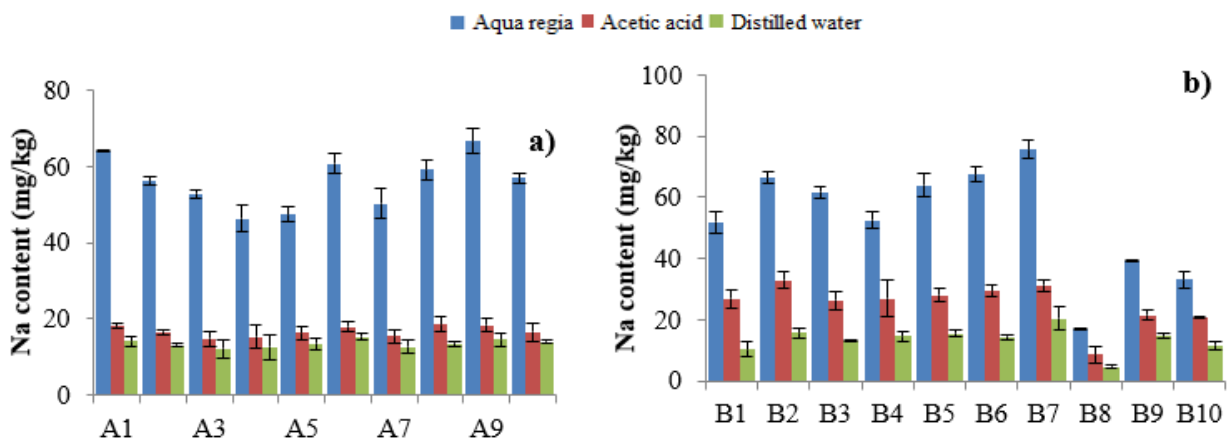
Regarding the value of the substitution acidity (5.78), which represents the exchange of ions from the adsorption complex of the soil (Minasny, McBratney, Brough *et al.*, 2011), with cations from the neutral salt (K<sub>2</sub>O and Ca) the difference between Ca and H<sub>2</sub>O (CaCl<sub>2</sub>x2H<sub>2</sub>O) with a value of 0.72 indicates moderate soil fertility. The same could be concluded with regard to the average value of the conductivity of soil samples “A”, which is 364 μS/cm. It can be related to soil depletion because a large number of crops have been sown in previous vegetation. The average substitution acidity for soil samples “B” is 5.94. According to the value of ΔpH for pH (H<sub>2</sub>O) and pH (CaCl<sub>2</sub>x2H<sub>2</sub>O) which is 0.77, the given soil is richer in exchangeable ions than the soil from the “A” location, which is additionally confirmed by the higher average conductivity value (Chen and Ma, 2016) in the given samples (568 μS/cm).

The determination of such soil properties, can refer to the influence of metal mobility (Šapčanin, Čakal, Jačimović *et al.*, 2017).

#### *Sodium concentrations extracted by various extraction agents - method of shaking*

Sodium concentrations measured after soil extraction from “A” by various extraction agents ranged from 12.29-66.55 mg Na/kg of soil (Figure 1(a) and Table 3). As can be seen, the highest results were obtained using aqua regia as an extraction agent. Aqua regia dissolves most metals, except those that are tightly bound in silicate soil minerals. Therefore, the content of Na extraction agent is referred to as pseudo-total content (Sung and Ozcan, 2014).

The values of the pseudo-total Na content in the specified soil sample “A” are in the range from 46.35-66.55 mg Na/kg of soil, where the values of standard deviations are ≤3.88 mg Na/kg soil. In the case of soil samples “B”, the values of Na content are in the range 17.15-75.66 mg Na/kg soil with standard deviations ≤3.81 mg Na/kg of soil. It is necessary to know the concentration of sodium in the soil because Na participates in the total ion exchange and is a useful indicator of soil fertility.



**Figure 1:** Comparative results of Na concentration (mg Na/kg of soil) in soil samples obtained using three different extraction agents assisted by the method of shaking for samples “A” (a) and “B” (b).

In contrast to the pseudo-total Na content, the bioavailable forms of sodium are determined using green solvents (5% CH<sub>3</sub>COOH acid and distilled H<sub>2</sub>O) and represent the values of Na that will be potentially available in the real conditions (Dočekalová, Kovaříková, Dočekal *et al.*, 2012). With 5% CH<sub>3</sub>COOH, the content of Na in the soil were in the range of 14.77-18.59 mg Na/kg of soil (±2.95 mg Na/kg of soil) and 20.87-32.80 mg Na/kg of soil, if samples B8.1 and B8.2 are excluded (±6.01 mg Na/kg of soil) for the samples of “A” and “B” location, respectively (Figure 1(b) and Table 4). Slightly higher results were obtained with 5%

CH<sub>3</sub>COOH, approximately by 15-22% and 46% higher results for samples “A” and “B”, respectively, compared to the results obtained by extraction with distilled water. In comparison to the values of the pseudo-total Na content in the soil samples, 5% CH<sub>3</sub>COOH could extract on average about 34% and 49% Na<sup>+</sup> ions in relation to its pseudo-total value from samples “A” and “B”, respectively. These results showed that the analyzed soils by chemical structure consists of easily available organic and inorganic forms in which the Na<sup>+</sup> ion is present.

In the case of distilled water as an extraction agent, the obtained Na values referred to the mobile fraction of sodium (Minkina, Motuzova, Mandzhieva et al., 2013; Slukovskaya, Kremenetskaya, Drogobuzhskaya et al., 2020) were in the range of 12.58-15.20 mg Na/kg of soil ( $\pm 3.29$  mg Na/kg of soil) and 4.62-20.33 mg Na/kg of soil ( $\pm 3.86$  mg Na/kg of soil) for soil samples "A" and "B", respectively.

According to the obtained results up to 25% of Na content could be extracted with distilled water from its pseudo-total content of the soil samples. Since the values of Na in the soil samples "A" obtained with acetic acid were not significantly higher compared to the use of distilled water (about 9%), there are not many weakly bound Na<sup>+</sup> ions to inorganic sites (carbonates).

Furthermore, relatively low values of standard deviations in all three cases indicated good Na homogeneity in the examined soils. In addition, obtained values with 5% CH<sub>3</sub>COOH were higher about 54% compared to the results obtained by extraction with distilled water from the "B" which is due to a higher proportion of loosely bound Na<sup>+</sup> ions for inorganic sites (carbonates).

**Table 3:** Mean values of the soil samples "A" for all three extraction agents used - shaking method

Samples	ISO (mg/kg)	CH <sub>3</sub> COOH (mg/kg)	H <sub>2</sub> O (mg/kg)
A 1.1; A	63.96±0.10	18.21±0.83	14.10±1.26
A 2.1; A	56.19±1.18	16.47±0.70	13.14±0.39
A 3.1; A	52.76±1.18	14.77±1.85	12.29±2.40
A 4.1; A	46.35±3.36	15.37±2.95	12.58±3.29
A 5.1; A	47.42±2.13	16.30±1.62	13.45±1.49
A 6.1; A	60.73±2.51	17.93±1.33	15.20±0.84
A 7.1; A	50.18±3.88	15.47±1.82	12.71±1.71
A 8.1; A	59.06±2.75	18.59±1.87	13.52±0.74
A 9.1; A	66.55±3.34	18.38±1.89	14.55±1.61
A 10.1; A	56.85±1.25	16.49±2.44	14.06±0.52

**Table 4:** Mean values of the soil samples "B" for all three extraction agents used - shaking method

Samples	ISO (mg/kg)	CH <sub>3</sub> COOH (mg/kg)	H <sub>2</sub> O (mg/kg)
B 1.1; B	51.83±3.47	26.91±2.96	10.36±2.32
B 2.1; B	66.32±1.74	32.80±2.76	15.58±1.68
B 3.1; B	61.32±1.85	26.21±2.82	13.05±0.46
B 4.1; B	52.50±2.89	26.79±6.01	14.58±1.50
B 5.1; B	63.93±3.81	27.90±2.28	15.44±1.05
B 6.1; B	67.37±2.44	29.39±1.76	14.21±0.59
B 7.1; B	75.66±3.21	31.09±1.83	20.33±3.86
B 8.1; B	17.15±0.17	8.55±2.65	4.62±0.74
B 9.1; B	39.39±0.30	21.52±1.70	14.72±1.02
B 10.1; B	33.01±2.76	20.87±0.30	11.55±1.44

Comparing the values of Na content in the soil suspensions from "A" and "B" location in the case of distilled and acetic acid as an extraction agent, it is obvious that the soil from "B" location is richer in

available forms of Na. This is in accordance with the fact that beef manure was used to fertilize the soil of the "B" location in the previous vegetation, and the number of sown crops was more modest compared to the soil from "A" location. Therefore, the soil from the "B" location remained richer in terms of available forms of Na, which can be extracted quite well with the green solvents used (distilled water and 5% CH<sub>3</sub>COOH). Table 3 and 4 shows overall results of all 10 samples of the tested soil from the "A" and "B", respectively, for all three extraction agents used.

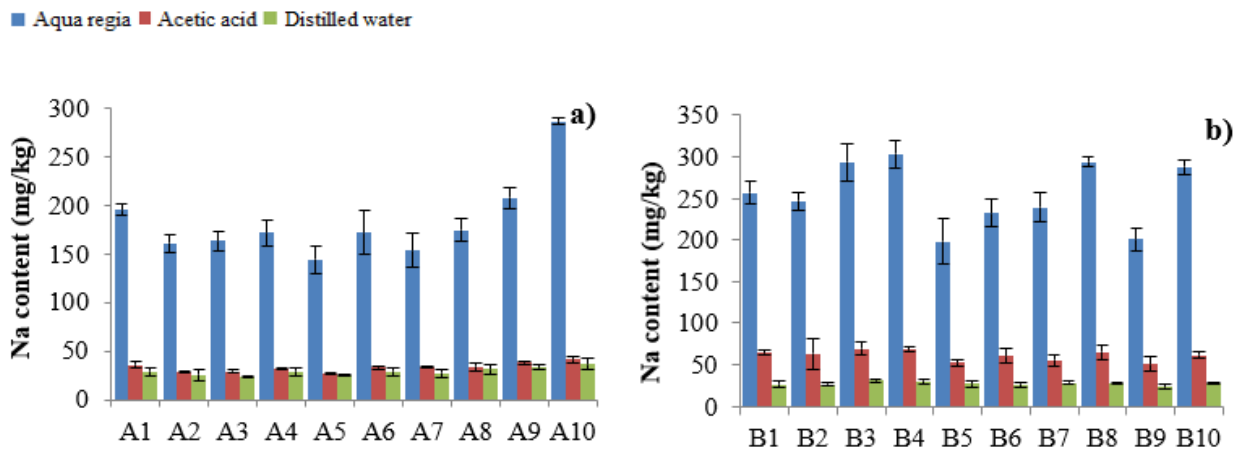
#### *Sodium concentrations extracted by various extraction agents - ultrasonic extraction*

Determination of Na concentration in the soil from "A" and "B" locations was also performed by applying ultrasound to soil extraction with three selected solvents (aqua regia, 5% CH<sub>3</sub>COOH and distilled water). The application of ultrasound was primarily aimed at controlling the pseudo-total Na content from the soil, and for 18 hours it can be extracted only by applying ultrasound to the same solvents for 2 hours. The obtained results are presented in Figure 2 as well as in Table 5 and 6.

The highest results (Figure 2a and 2b) were obtained with aqua regia, followed by 5% CH<sub>3</sub>COOH and distilled water, which is the same trend as in the case of shaking extraction. However, it can be noticed that significantly higher concentrations of Na were obtained by ultrasound in the tested soil, for all samples, and the difference is especially significant when aqua regia is used as a solvent.

Furthermore, using ultrasound to extract Na from soil samples with 5% CH<sub>3</sub>COOH and distilled water, it could be seen that the results for samples "A" were almost similar and close, regardless of the solvent. In the case of soil samples "B", the Na content using 5% CH<sub>3</sub>COOH and distilled water is more significant, due to the fact that there are more available forms of Na<sup>+</sup> ion, as well as the fact that the soil was less sown. According to the presented results, with distilled water it is possible to extract 17%, while with 5% CH<sub>3</sub>COOH only 22% of its pseudo-total content in the soil from the "A" location, which is in the range of 153.3-285.6 mg/kg soil. The maximum standard deviations are 22.98, 4.79 and 6.28 mg/kg in the case of using aqua regia, 5% CH<sub>3</sub>COOH and distilled water, respectively.

Regarding the results of extractions of soil samples "B", the following intervals for sodium content are recorded, as follows: from 198.5-303.2 mg/kg; from 50.53-68.99 mg/kg and from 23.31-30.64 mg/kg when aqua regia, 5% CH<sub>3</sub>COOH and distilled water were used as extraction agent, respectively. In relation to the pseudo-total sodium content in the mentioned soil, 26% can be extracted with 5% acetic acid and 13% with distilled water. The maximum standard deviations are 27.56, 18.34 and 4.43 mg/kg for extraction carried out with aqua regia, 5% CH<sub>3</sub>COOH and distilled water, respectively.



**Figure 2:** Comparative results of Na concentration (mg Na/kg of soil) in soil samples obtained using three different extraction agents assisted by the method of ultrasound for samples "A" (a) and "B" (b).

**Table 5:** Mean values of the soil samples "A" for all three extraction means used - application of the ultrasound method

Samples	ISO (mg/kg)	CH <sub>3</sub> COOH (mg/kg)	H <sub>2</sub> O (mg/kg)
A 1.1; A 1.2	195.1±5.5	35.64±3.35	28.79±3.83
A 2.1; A 2.2	160.4±8.4	28.27±0.69	25.18±5.19
A 3.1; A 3.2	163.1±9.8	29.02±2.02	23.58±1.04
A 4.1; A 4.2	171.2±13.2	31.68±0.66	29.01±4.09
A 5.1; A 5.2	143.8±14.5	27.05±1.05	25.51±0.82
A 6.1; A 6.2	171.7±23.0	32.80±1.27	28.62±4.10
A 7.1; A 7.2	153.3±17.1	33.90±1.13	27.07±4.05
A 8.1; A 8.2	174.3±11.7	33.57±4.79	31.19±5.34
A 9.1; A 9.2	207.3±11.1	37.64±2.00	32.86±2.66
A 10.1; A	285.6±3.4	41.14±2.75	36.43±6.28

**Table 6:** Mean values of the soil samples "B" for all three extraction means used - application of the ultrasound method

Samples	ISO (mg/kg)	CH <sub>3</sub> COOH (mg/kg)	H <sub>2</sub> O (mg/kg)
B 1.1; B 1.2	256.6±13.4	64.36±2.54	26.30±3.48
B 2.1; B 2.2	247.2±22.4	63.33±18.34	26.55±1.10
B 3.1; B 3.2	294.1±22.4	68.99±7.57	30.64±1.86
B 4.1; B 4.2	303.2±17.2	68.59±4.18	30.00±2.76
B 5.1; B 5.2	198.5±27.6	52.21±3.71	26.75±4.43
B 6.1; B 6.2	232.0±16.3	60.41±8.47	25.75±3.43
B 7.1; B 7.2	239.4±18.4	55.35±7.10	27.86±2.00
B 8.1; B 8.2	294.2±6.2	64.30±8.36	28.54±0.94
B 9.1; B 9.2	200.6±13.9	50.51±9.13	23.31±2.40
B 10.1; B	287.6±9.5	61.54±4.20	27.52±1.28

In the studies published on ultrasonic assisted extraction of metals, some controversial results on the behavior of metals during extraction have been reported. In the work of Väisänen and co-workers (2001) ultrasound-assisted extraction method and the method by reflux with aqua

regia resulted in almost equal Ag, As, Cd, Cu, and Pb concentrations in soil.

Ultrasonic treatment can also cause the release of lower amounts of metal such as Ni in the exchangeable metal soil fraction in comparison to the conventional procedure. These results are probably due to the re-adsorption of metals on the surface of soil during the extraction step, which is enhanced by the application of ultrasound (Leśniewska, Krymska, Świerad *et al.*, 2016). However, acid type and the concentration in the liquid extractant seems to be one of the most critical parameters affecting ultrasound leaching (Güngör and Elik, 2007) as well as the length of time and power used in sonication (Davidson and Delevoye, 2001).

*Correlation analysis of sodium content determined by different extraction agents*

*a) method of shaking*

To determine the correlation of Na content from soil samples of "A" and "B" locations with different extraction agents applying the shaking method the conclusion was made from the mean value of two parallels for all 10 subsamples of each of the tested soil. In all samples, the results of Na content in the soil obtained by extraction with 5% CH<sub>3</sub>COOH compared to the extraction with the aqua regia are significantly lower on average 70% for soil samples "A" and 50% for soil samples "B" (Table 3 and 4).

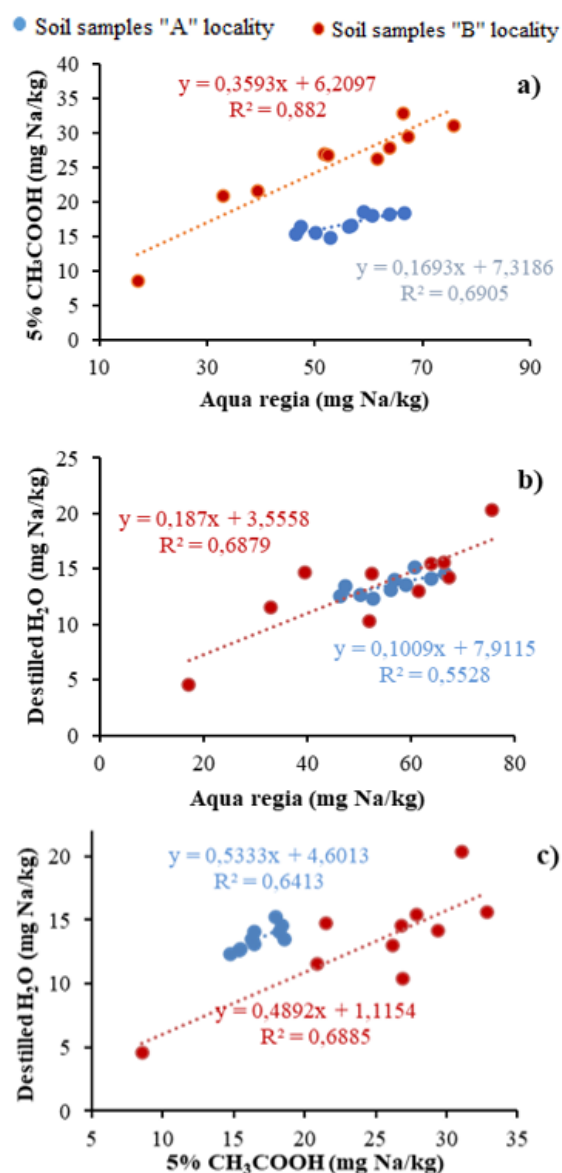
However, taking into account the comparative analysis for aqua regia and 5% CH<sub>3</sub>COOH (Figure 3a), there is a statistically very significant correlation,  $r^2=0.83$  for the soil from "A" and  $r^2=0.94$  for the soil from "B" location.

The obtained correlation values for both soil types indicate a high degree of correlation of numerical indicators of Na<sup>+</sup> ion content in the examined soil with different extraction agents, i.e. the increase in available forms of sodium is directly related to the increase in pseudo-total Na content in the soil. The relationship between the Na content in the soil and its water-soluble forms (extraction in distilled water) in relation to its pseudo-total content in is presented in Figure 3b. As in the previous case, the results of soil extraction with distilled water are significantly lower, on average 75% lower in the case of soil samples "A", than the results of soil extraction by aqua regia with a statistically slightly lower, but very significant positive correlation ( $r^2=0.74$ ). The same interpretation can be considered for soil samples "B", where a statistically significant positive correlation was confirmed ( $r^2=0.83$ ). Furthermore, due to similar results using 5% CH<sub>3</sub>COOH and distilled water for both soil samples a correlation analysis was performed for these two solvents to exclude an experimental error.

The obtained correlation analysis is shown in Figure 3c. Although the results of extraction with distilled water are slightly lower compared to the results of extraction with 5% CH<sub>3</sub>COOH, a statistically very significant positive correlation was found for the soil samples "A" and "B" of  $r^2=0.80$  and  $r^2=0.83$ , respectively, which excluded the experimental error. These data suggests that the tested soil has a chemical composition whose available forms of sodium are mostly used, so the increase in Na content with 5% CH<sub>3</sub>COOH is only about 20% higher for soil from "A" location. However, in terms of soil results from the "B" location, a slightly more positive effect of acetic acid on Na<sup>+</sup> ion extraction was observed since the obtained values were on average 50% higher compared to the extraction of the same soil with distilled water. This is in accordance with the fact that the soil examined from the "A" location was sampled after the soil was used for sowing, so it is poorer in the available forms of the determined metal.

#### b) method of ultrasound

The correlation analysis for the method of ultrasound and different extraction agents was carried out in the same way as by applying the shaking method of soil samples. The obtained correlation graphs are shown in Figure 4. Although the values of extractions along the aqua regia are 5.5 and 6 times higher for soil samples "A" and "B", respectively, compared to the results when 5% CH<sub>3</sub>COOH is used, in both cases a statistically significant positive correlation was obtained ( $r^2=0.87$  soil "A" and  $r^2=0.90$  soil "B").

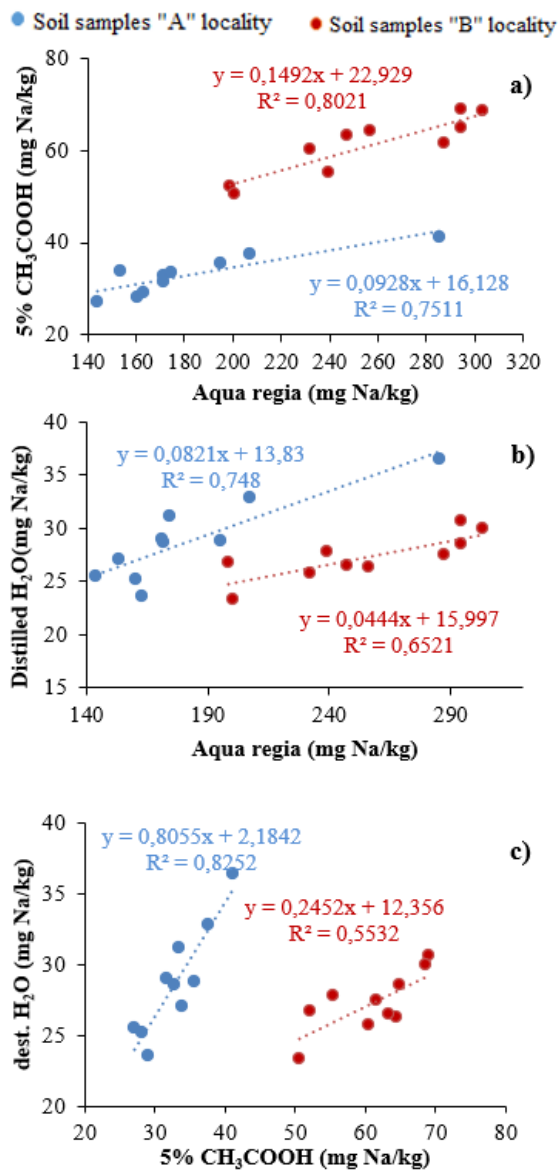


**Figure 3:** Correlation analysis of Na content (mg/kg of soil) obtained by extraction with aqua regia and 5% CH<sub>3</sub>COOH (3a); aqua regia and distilled water (3b); 5% CH<sub>3</sub>COOH and distilled water (3c) by shaking method.

According to the results shown in Figure 4a and 4b, it can be concluded that a significant positive statistical correlation was obtained, with  $r^2=0.86$  for soil samples "A" and  $r^2=0.81$  for soil samples "B". Since the results with CH<sub>3</sub>COOH and distilled H<sub>2</sub>O obtained by ultrasonic extraction do not differ significantly, a correlation analysis was applied and the results were shown in Figure 4c.

For soil samples of "A" location, with 5% CH<sub>3</sub>COOH, on average, up to 13% higher results were obtained, which is up to 4.25 mg Na/kg of soil. However, in terms of correlation analysis, a significant positive statistical correlation can be stated since  $r^2=0.91$ , thereby rejecting an experimental error. Additionally, 5% acetic acid is not a strong enough extraction agent that even with ultrasonic waves is not able to significantly extract the more strongly bound forms in which sodium occurs.

Contrary wise 5% CH<sub>3</sub>COOH extracted on average 55% more sodium regarding to the distilled water as solvent from the samples of "B" location. However, in terms of correlation analysis, a slightly lower but still significant positive correlation was obtained with  $r^2=0.74$ .



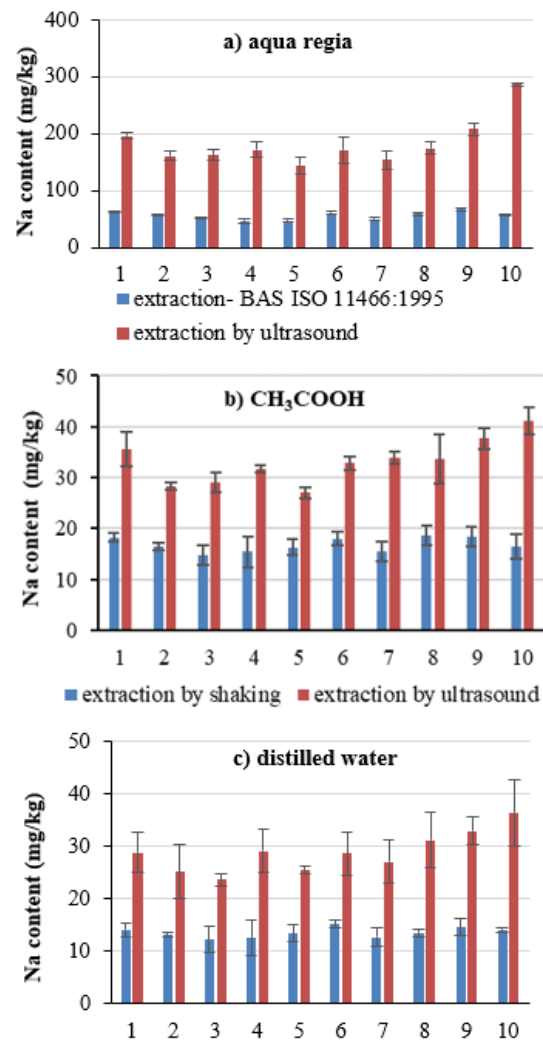
**Figure 4:** Correlation analysis of Na content (mg/kg of soil) obtained by extraction with aqua regia and 5% CH<sub>3</sub>COOH (4a); aqua regia and distilled water (4b) 5% CH<sub>3</sub>COOH and distilled water (4c) by ultrasound method

From all the above, it can be concluded that the increase in the value of water-soluble forms of Na<sup>+</sup> ion as well as its forms soluble in slightly acidic conditions, such as 5% CH<sub>3</sub>COOH is directly related to the increase of its pseudo-total content in soil. Also, a positive effect of 5% CH<sub>3</sub>COOH as a green solvent can be noted, as well as the influence of ultrasound on the extractability of Na<sup>+</sup> ions from the soil.

As reported by Chen and Ma (2001), the amount of trace element extracted by common digestion methods might depend on the element analyzed, its origin (anthropogenic or natural), soil properties and element mass fraction.

Comparison of sodium content obtained by different extraction methods

Figures 5-6 present comparative results of Na content in soil from the "A" and "B" location obtained with aqua regia, 5% CH<sub>3</sub>COOH and distilled water, using two extraction methods (shaking method and ultrasonic extraction). The extraction with aqua regia in the first case was performed according to the procedure BAS ISO 11466:1995, and not with shaking. The results are given as the mean of two determinations with a standard deviation of repeatability.

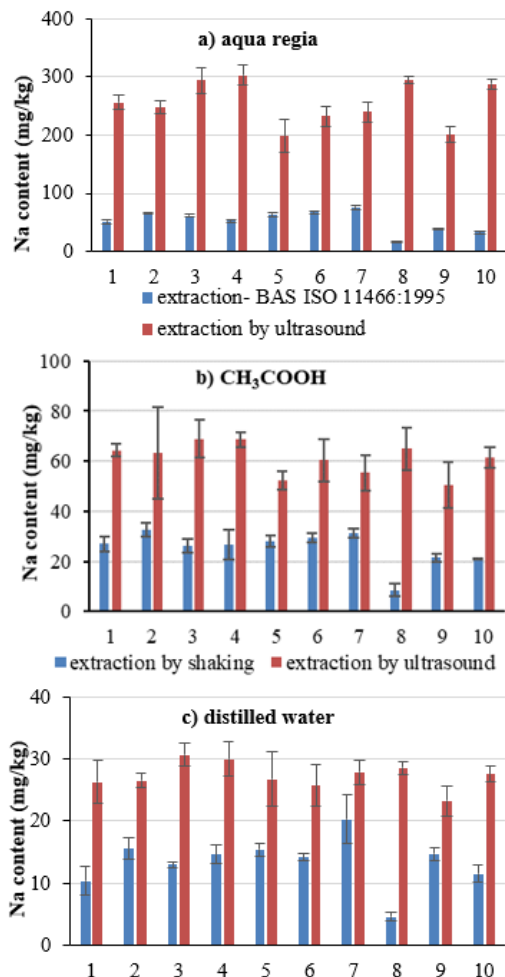


**Figure 5.** Comparative presentation of Na content (mg/kg of soil) obtained according to BAS ISO 11466: 1995 (or shaking method) and ultrasonic extraction with aqua regia (a); CH<sub>3</sub>COOH (b) and distilled water (c) for soil from the soil samples of "A" location.

The efficiency of ultrasound extraction was evaluated by comparing the results obtained using the ultrasonic method with the results of the standard BAS ISO method shown in Figure 5. Analyzing the obtained results, a positive effect of ultrasound on the extractability of Na<sup>+</sup> ions from soil samples can be found since the obtained results are on average 3 times higher (from 143.78 to 285.63 mgNa/kg of soil) than when extraction is performed without the use of ultrasound (from 46.35 to 66.55 mg Na/kg of soil). Also, an important factor is the duration of extraction, which using the BAS ISO method



without ultrasound lasted a full 18 hours, while using the same extraction agents with ultrasound, the extraction lasted only 2 hours. These data, therefore, favors the use of ultrasound to extract  $\text{Na}^+$  ions from soil samples, as significantly higher results were achieved in a shorter time, and the use of ultrasound is considered a non-destructive method of sample preparation.



**Figure 6:** Comparative presentation of Na content (mg/kg of soil) obtained according to BAS ISO 11466: 1995 (or shaking method) and ultrasonic extraction with aqua regia (a);  $\text{CH}_3\text{COOH}$  (b) and distilled water (c) for soil from the soil samples of "B" location.

Regarding soil samples "B" (Figure 6), where a higher proportion of soluble forms of Na was previously found, the application of ultrasound was more effective with the use of aqua regia, with the ultrasound/BAS ISO extractability ratio being 6 times higher on average.

According to the results, the ratio of Na content by shaking/ultrasound method with 5%  $\text{CH}_3\text{COOH}$  as an extraction agent is 2, i.e. 3 times higher with ultrasound for soil from "A", i.e. "B" location, respectively. Furthermore, the ratio of Na content by the method of shaking/ultrasound with distilled water as extraction agent was 2, i.e. 2.5 times higher with ultrasound for soil from the location "A", i.e. "B" respectively.

Ultrasound can significantly improve the extraction efficiency mainly due to the effects caused by the cavitation phenomenon (Stanišić et al., 2011, Diehl et al., 2018), which is confirmed by this study. Since insufficient data could be found in the literature for the solubility of sodium ions from soil samples by ultrasonic methods, these results were very significant.

## CONCLUSION

The soil sample "A" belongs to the type of alluvial soil and was fertilized with burnt manure, while soil sample "B" belongs to the type of clay loam fertilized with beef manure. According to the average pH value in distilled water, the analyzed soil samples ("A" and "B") were classified as neutral and weakly acidic soils, while pH in  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and electrical conductivity show more exchangeable ions for soil samples "B". Up to 25 % and 26% can be extracted with distilled water, while up to 34 % and 49% with 5 %  $\text{CH}_3\text{COOH}$  by shaking samples in relation to the values of its pseudo-total content from soil samples "A" and "B", respectively. An increase in the value of water-soluble and available forms of sodium was found with an increase in the value of the pseudo-total sodium content in the soil, whereby correlation coefficients  $r^2 \geq 0.74$  were obtained for all comparison models. Ultrasound yielded significantly higher Na concentrations for both analyzed soils compared to the shaking method, and the difference is especially significant when aqua regia is used as a solvent. Extraction with aqua regia and ultrasound gave results on average 3 times higher than when extraction is performed without the use of ultrasound for "A" soil samples and on average 6 times higher for soil samples "B". The content ratio of the ultrasonic/shaking method with 5%  $\text{CH}_3\text{COOH}$  as extraction agent is 2 or 3 times higher for soil samples "A", i.e. "B", respectively.

In the case of distilled water as an extraction agent, the effect of ultrasound gave 2 and 2.5-times higher results for soil samples "A" and "B", respectively, compared to the method of shaking. In general, the application of ultrasound shows a positive effect on the extractability of  $\text{Na}^+$  ions from soil samples "A" and "B" using green solvents (distilled water, 5%  $\text{CH}_3\text{COOH}$ ) but also with the use of a strong extraction agent such as aqua regia. Therefore, the use of ultrasound is preferred in order to improve the extractability of  $\text{Na}^+$  ions from soil samples, and, in addition, due to the fact that the use of ultrasound is considered a non-destructive method of sample preparation.

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### Summary/Sažetak

U ovoj studiji analizirani su uzorci tla s dva odabrana mjesta: "A" (aluvijalno tlo) i "B" (glinena ilovača). Hemijska analiza uzoraka tla uključivala je: određivanje pH vrijednosti tla i provodljivosti tla. Dvije različite metode ekstrakcije: metoda treskanja i metoda ultrazvuka primijenjene su za ekstrakciju natrijevih iona iz tla s tri otapala (aqua regia, 5% CH<sub>3</sub>COOH i destilirana voda). Vrijednosti pseudo-ukupnog (ekstrahovano sa aqua regia) i bioraspoloživog sadržaja Na (ekstrahovanog sa 5% CH<sub>3</sub>COOH i destilovanom vodom) u uzorku tla "A" su u intervalu od 46,35-66,55 mg Na/kg; 14,77-18,59 mg Na/kg i 12,58-15,20 mg Na/kg tla, primjenom metode treskanja. Istom metodom, u slučaju uzorka tla „B“, intervali su 17,15-75,66 mg Na/kg; 20,87-32,80 mg Na/kg i 4,62-20,33 mg Na/kg tla, za ekstrakciju aqua regiom, 5% CH<sub>3</sub>COOH, odnosno destiliranom vodom. Ekstrakcija ultrazvukom u svim slučajevima dala je bolje rezultate u odnosu na metodu treskanja. Općenito, primjena ultrazvuka pokazuje pozitivan efekat na ekstrakciju iona Na<sup>+</sup> iz uzoraka tla pomoću spomenutih otapala.

