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The mobility of arsenic and its species in selected herbs

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Abstract: The aim of the study was verification of the response of chamomile (*Matricaria recutita (L.) Rauschert*), peppermint (*Mentha x piperita*) lemon balm (*Melissa officinalis L.*), and sage (*Salvia officinalis L.*) on the elevated contents of inorganic As species in soils. The ability of herbs to accumulate arsenic was tested in pot experiment in which soils were contaminated by As(III) and As(V). The As(III), As(V), AB (arsenobetaine), MMA (monomethylarsonic acid) and DMA (dimethylarsinic acid) ions were successfully separated in the Hamilton PRP-X100 column with high performance-liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) techniques. The study examined total arsenic contents in soil and plants, as well as the mobility of the arsenic species from the soil into the studied plants. Peppermint demonstrated the highest arsenic concentration and phytoaccumulation among studied plants. The sequential chemical extraction showed that arsenic in the contaminated soil was mainly related to the oxide and organic-sulfide fractions. The results showed that the oxidized arsenic form had a greater ability to accumulate in herbs and was more readily absorbed from the substrate by plants. Research has shown that soil contaminated with As(III) or As(V) has different effects on the arsenic content in plants. The plant responses to strong environmental pollution varied and depended on their type and the arsenic species with which the soil was contaminated. In most cases it resulted in the appearance of the organic arsenic derivatives.

Introduction

Herbs are traditionally used in folk medicine and play an important role in general human health condition (Liu et al. 2013, Sun et al. 2004, Xie et al. 2006, Yuan et al. 2007). Typically, they do not exhibit strong effect and do not cause side effects. Their therapeutic activity is related to the contents of organic components such as alkaloids, tannins, essential oils, and vitamins. Herbs are an important link in the transfer of trace elements from the soil to the human body (Agostini et al. 2009, Conforti et al. 2008, Pytlakowska et al. 2012). Plants such as peppermint (*Mentha x piperita*), chamomile (*Matricaria recutita (L.) Rauschert*), lemon balm (*Melissa officinalis L.*), and sage (*Salvia officinalis L.*) are the most commonly used herbs in medicine, food industry, and herbal products. These herbs are very popular in Poland and are present in almost every household. They are consumed because of their taste and are used routinely in many ailments. Herbal products are an increasingly popular form of the complementary and alternative medicine. The consumers are persuaded that these products are natural, safe, affordable, and free from negative influences.

However, as research has shown, these products can be toxic due to their plant composition, falsifications associated with the addition of synthetic agents, or the content of toxic metals and non-metals at dangerous levels (Esmaeili et al. 2006, Hedegaard et al. 2013). Herbal products are often bought in pharmacies. Nevertheless, they are not subject to the legislative drug regulations. Their manufacturers solely need to register them before sale and put their composition on the label.

Arsenic is a toxic metalloid common in the environment and various biological systems (Seńczuk 1990). Arsenic toxicity depends not only on its total content, but also on the concentrations of its individual species. In principle, speciation is important not only in the case of As, but also for many other elements (Hg, Pb, Se, etc.). Therefore, determining the total arsenic concentration is not sufficient to evaluate the risk associated with this element.

As the industrial pollution has not been reduced in recent decades, the arsenic emission from the industry, steelworks, animal waste, and dust from the fossil fuel combustion is currently rising. As arsenic is very mobile, it occurs in all the environment components. However, its inorganic species (As(III) and As(V)) are about 100 times more toxic than the organic ones (MMA – monomethylarsonic acid, DMA – dimethylarsinic acid, AB – arsenobetaine). From inorganic As species, arsenites are more toxic than arsenates. The contents of toxic species of

As in the environment are still increasing, due to the industrial development and economic growth. In Polish rivers, the content of As(III) in water was even 2.36 $\mu g \cdot L^{-1}$ in the Kłodnica River (Jabłońska-Czapla 2015a) or 3.83 $\mu g \cdot L^{-1}$ in the Biała Przemsza River (Jabłońska-Czapla 2015b).

Human exposure to arsenic can cause various detrimental health effects, such as dermatological, pulmonary, cardiological, genetic, genotoxic or mutagenic (Selene et al. 2003). For humans, water and food are the main arsenic sources. When compared to its inorganic forms, the organic compounds of As are relatively non-toxic to humans. Inorganic arsenic forms are metabolized in the human body to their methylated species (in the methylation process) and removed at least partly, together with urine (Vahidnia et al. 2007).

The application of hyphenated techniques such as high performance-liquid chromatography-inductively coupled plasma-mass spectrometry (HPLC-ICP-MS) allows for speciation analysis (Cai et al. 2017, Das et al. 2001, Donner et al. 2017, Hong et al. 2018, Jabłońska-Czapla et al. 2014a, Jabłońska-Czapla et al. 2015, Jabłońska-Czapla 2015b, Marcinkowska et al. 2016, Templeton et al. 2000, Zheng et al. 2003). It is necessary for the hyphenated methods used in the arsenic speciation analytics (at low concentration levels) to be both appropriately selective and sensitive (Hong et al. 2018). In the literature there are many studies on the instrumental methods used for the speciation of arsenic chemical species. Most of them are based on the chromatographic separation techniques, such as HPLC (Asaoka et al. 2012, Cornelis et al. 2003, Ellis and Roberts 1997, Moldovan et al. 1998, Pantsar-Kallio and Manninen 1997, Roig-Navarro et al. 2001, Ronkart et al. 2007).

Fractionation is a method enabling differentiation of operationally defined element forms, while the sequential extraction procedure allows to separate trace metals into chemical forms that can be released into the solution under different environmental conditions. One of the most frequently used types of sequential extraction is either the extraction scheme suggested by the Institute for Reference Materials and Measurements (BCR) (Tokalioglu et al. 2003) or Tessier's chemical extraction procedure (Tessier et al. 1979).

Plants growing on polluted substrate absorb metals and metalloids (Pavlovic et al. 2006, Ruzickova et al. 2015, Voyslavov et al. 2013, Zheljazkov and Nielsen 1996, Zheljazkov et al. 2006, Zheljazkov et al. 2008a, Zheljazkov et al. 2008b, Zurayk et al. 2001). Plants partially metabolize arsenic into its methyl species. Due to the easiness of arsenic accumulation in plants (Samecka-Cymerman and Kempers 2000), its toxicity and plant tolerance for this element, the number of speciation study were carried out in: *Acer platanoides* (Budzyńska et al. 2018), *Pteris vittata* (Wang et al. 2002), radish (*Raphanus sativus*) (Tlustos et al. 2002), bean (*Phaseolus vulgaris*) (Sukanya et al. 2018) and even *Xerocomus badius* (Niedzielski et al. 2013). However, the As transformations in mushrooms are different from the higher plants (Kalač 2010).

The proportional dependence of the arsenic content in plants on the presence of soil indicates a passive mechanism. The plant uptake of arsenic depends strongly on the plant species and soil physicochemical conditions. In the case of a substrate (or air) contamination with arsenic compounds, its content in plants increase even up to several thousand $mg \cdot kg^{-1}$ (Niedzielski et al. 2000, Koukamp et al. 2016). Inside plants, as arsenic speciation analysis showed, As can affect growth and productivity due to a plethora of morphological, physiological, biochemical, and molecular alterations (Abbas et al. 2018). Unfortunately, there is little research in the world literature on the arsenic speciation in herbs, which are very popular, eagerly consumed, and collected from contaminated areas. Arsenic from the soil can be absorbed and stored in plants growing on such a substrate. Its migration from the soil into the plant tissues is a key step in the process of food contamination with the element. Although the migration rates of arsenic from the soil to many plants have already been investigated, the research on the dynamics of its occurrence in the soil and its migration and absorption by herbs such as peppermint (*M. x piperita*), chamomile (*M. recutita*), lemon balm (*M. officinalis*), and sage (*S. officinalis*) is limited. The World Health Organization (WHO) recommends that the daily arsenic dose in food should be 0.05–12.46 µg per day for total arsenic and 0.21–0.83 µg per day for its inorganic form (Kabata-Pendias and Pendias 1999).

In the present study the concentration of As including organic [MMA(V), DMA(V), AB] and inorganic (As(III), As(V)) arsenic forms in leaves and steams of selected herbaceous plants was investigated. Selected herbs are used in the production of herbal teas and other dietary supplements. In our experiment, the ability of four herbs to accumulate potential risk element was tested in a pot experiment in which soil was contaminated by different arsenic species (As(III) and As(V)). The study was also conducted to demonstrate how soil contamination with inorganic arsenic species (As(III) or As(V)) affected the content of organic and inorganic forms of this metalloid in selected herbs.

The main objectives of the experiment were i) to verify the tolerance of chamomile, peppermint lemon balm, and sage plants to increased risk element contents in soil which can be affected by various arsenic species contamination, ii) to estimate the potential risk of increased arsenic contents for herbs production as a medicinal plants as well as possibility of herbs cultivation in arable soil contaminated with arsenic, and iii) to find relationship between the content of arsenic species in soil and the corresponding herbaceous plants.

Materials and methods

Sample preparation

In the study plants i.e. chamomile (*M. recutita*), peppermint (*M. x piperita*), lemon balm (*M. officinalis*), and sage (*S. officinalis*), were planted (May 2015) in isolated containers. The soils in the containers were enriched with appropriate inorganic As(III) and As(V) species. The soils were contaminated in such a way that 2 $g \cdot L^{-1}$ of the appropriate arsenic form was added to 9.8 kg of soil. Thus, the arsenic concentration of approx. 200 $mg \cdot kg^{-1}$ in the soil was obtained. The control samples were also planted (plants growing on the same but not enriched soil). The plant samples were collected at the vegetation peak. After sampling they were washed with deionized water and separated into stems and leaves. For comparative purposes, commercially available herbal teas were purchased at the pharmacy: chamomile fix, peppermint fix, sage fix, lemon balm fix. Samples of herbal teas (fix) were prepared as plant samples.

Reagents and standard solutions

The following substances were used for analyses: dihydro sodium arsenate heptahydrate ACS reagent (Sigma-Aldrich, Spain), sodium arsenite purum p.a. ≥99% (Sigma-Aldrich, Sweden), disodium methyl arsenate analytical standard (Supelco, USA), arsenobetaine ≥95% NMR (Fluka), dimethylarsinic (Supelco, USA), ultrapure nitric acid (65%, Merck, Germany), ultrapure ammonium nitrate (Merck, Germany). The calibration solutions were prepared each time through diluting suitable standard solutions on an analytical balance. The multi-elemental standards no. XXI and VI (Merck, Germany) were used when determining total arsenic and other metal(loid)s with ICP-MS. The ICP-MS spectrometer was optimized daily with a 10 $g \cdot L^{-1}$ solution (Mg, Cu, Rh, Cd, In, Ba, Ce, Pb, U) in 1% HNO_3 Elan 6100 Setup/Stab./Masscal. Solution (Perkin-Elmer). All solutions and standards were prepared with the Milli-Q-Gradient ultrapure deionized water (Millipore, Merck, Germany), whose electrolytic conductivity was <0.05 $\mu S \cdot cm^{-1}$.

Analytical method applied

The basic physicochemical soil tests such as: sieve analysis (PN-ISO 11277:2005), pH, Eh and conductivity measurements (PN-ISO 10390:1997), total arsenic determinations in the soil, and plant digest (PN-EN ISO 17294-2:2016-11), and speciation analysis of arsenic in the plant extracts were conducted. For the basic research, a multi-parameter CX-401 meter (Elmetron, Poland) equipped with a glass ERH 111 electrode (Hydromet, Poland), platinum ER Pt-111 electrode (Hydromet, Poland), conductometric CD-2 sensor with a built-in thermometer (Hydromet, Poland) were used.

The total As, Mn, Co, Ni, Cu, Zn, Cd, Pb, Cr, Ba and Ag contents was determined with an ICP-MS Elan 6100 DRC-e spectrometer. The spectrometer was equipped with a quartz torch, cross-flow nebulizer (0.76–0.82 $L \cdot min^{-1}$), and nickel cones. For the arsenic speciation study HPLC-ICP-MS, the Perkin Elmer series 200 speciation system and ICP-MS Elan 6100 DRC-e spectrometer were used. HPLC-ICP-MS system was equipped with Hamilton PRP-X100 (150 mm × 4.6 mm, particle size=5 µm) column. Gradient elution was used with A: 20 mM NH_4NO_3 (pH=8.7) and B: 60 mM NH_4NO_3 (pH=8.7) eluents. The AB, As(III), DMA, MMA and As(V) ions were separated with retention time: 1.84, 2.16, 2.95, 5.36, 6.17 min., respectively.

Sample preparation for the determination of the total element contents

In order to determine total arsenic and other metal/metalloid contents in 1-g soils samples, the microwave digestion (with the CEM Corporation MARS X Digestion Microwave System) was used. The soil digestion was performed with the following reagents: 6 ml nitric acid + 2 ml hydrogen peroxide + 2 ml hydrofluoric acid. The digestion program had the following parameters: 1,400 W, 15 min to 240°C (stop time: 30 min). Afterwards, they were washed with deionized water, cut, air-dried and ground in a porcelain mortar to homogenize stems and leaves separately. In order to determine total arsenic contents in the 0.1–0.15 g plant samples, the digestion in a microwave oven (Anton Paar 2000 oven) was carried out with the following reagents: 5 ml of spectrally pure nitric acid + 3 ml of water. Arsenic and other element contents in the plant and soil digest were determined by ICP-MS spectrometry.

According to Tessier et al. (1979) extraction procedure six individual fractions were distinguished: F0 – water-soluble metal fraction, F1 – exchangeable fraction, F2 – acido-soluble fraction, F3 – reducible fraction, F4 – oxidisable fraction, F5 – residual fraction. Chemical reagents and analytical conditions for the sequential extraction procedures are presented in earlier work (Jabłońska-Czapla et al. 2014b).

Validation parameters

The parameters such as the detection limit, recovery or uncertainty are given in Table 1. The simultaneous analysis of inorganic and organic arsenic ionic forms was validated with certified reference materials for water (NIST 1643-e) and plant (NIST Tomato Leaves 1573a), and standard addition method. Unfortunately, certified reference materials contained only information on the total arsenic and other total element contents.

The limit of detection (LOD) for arsenic species and method repeatability were calculated with the multiple calibration curves. For specific analytes, the LODs were between 0.08 $\mu g \cdot L^{-1}$ (As(III)) and 0.16 $\mu g \cdot L^{-1}$ (AB). The standard deviation values were determined as a standard deviation for a free factor of the obtained calibration curve. The measurement uncertainty (understood as Type A uncertainty) was determined with multiple measurements of diversified real samples (n>30). The uncertainty expressed in [%] did not exceed 17% for arsenic ions. The method recovery was established with measurements of the real samples to which the known amount of a specific analyte was added. The recovery values ranged from 96% (As(III)) to 104% (As(V)). Certified reference materials NIST Tomato Leaves 1573a was digested together with the samples, obtaining 102% arsenic recovery and extracted with water:methanol (in a ratio 1:9), with 41.7% extraction efficiency.

The carrier gas, argon in the ICP-MS technique, readily and easily forms polyatomic ions, such as $^{40}Ar^{35}Cl$, which can cause several spectral interferences. Chlorine together with argon can have a significant impact on the arsenic speciation analysis result. For this reason, the separation conditions in the HPLC-ICP-MS system were chosen in such way that the peak derived from this interference appeared in the chromatogram with the retention time different from the retention time for the tested arsenic forms. Figure 1 shows an example of a sample containing all arsenic species together with a peak originating from the $^{40}Ar^{35}Cl$ interference. The extraction efficiency was also checked.

Based on the in-depth literature analysis, the extraction of plant samples was not optimized and the wide spectra of extraction methods were already published. However, a method offering the highest arsenic extraction yield from the samples of the plant origin was selected (Zheng et al. 2003). The extraction of 1-g plant material in 10 ml of water:methanol solution in a ratio 1:9 was used. The HPLC-purity methanol was used. Each sample was extracted with 2-hour shaking in a shaker (165 rpm). The extracted plant samples underwent filtration through a 0.22-µm syringe filter and were injected into the HPLC-ICP-MS system for the arsenic speciation analysis.

Arsenic phytoaccumulation coefficient

The phytoaccumulation coefficient describes the plant ability to absorb metals from the soil in relation to the migration

load size (Rajfur 2015). The factor is useful for assessing the plant contamination with a given metal in relation to the sum of its bioavailable form contents in the soil, in this case the calculation of WF was made from the total As content. The phytoaccumulation coefficient is calculated with the following formula: WF=C1/C2; where C1 is the metal concentration in the plant; and C2 is the metal concentration in the soil. When the coefficient is less or equal to 0.01, the metal accumulation does not occur in the plant. The coefficient describes a weak degree of the metal accumulation in the plant when its value is less or equal to 0.1. The average accumulation is described by WF≤1.0, while the intensive metal accumulation degree in the plant occurs when WF>1.0.

Results and discussion

pH, Eh, conductivity, and particle size soil analyses

The size (sieve) analysis showed that the fractions of fine gravel (5.0–2.5 mm) and sand (2.0–1.0 mm and 1.0–0.5 mm) were predominant in the soil utilized in the research. The basic physicochemical parameters of soil are presented in Table 2. The soil pH increased after the growing season both for the control (non-contaminated) and contaminated soils. The granulometric analysis allowed to conclude that the fine gravel and sand fractions were predominant in the test soil. The basic physicochemical investigations showed that the soil pH ranged from 7.1 to 7.4; Eh was 190.2–195.9 mV; and conductivity had values of 2.55–2.96 mS·cm^{-1}.

As it is well known, the mobility of metals and metalloids in soils is influenced by pH and Eh. Soil pH is considered one of the most important factors determining the concentration of metals in the soil solution, their mobility and availability to plants. The increase of hydrogen ion concentration affects the mobilization intensity of heavy metals. In highly acidic soils, the mobility of metallic elements is much higher than in soils with neutral and alkaline reaction (Fijalkowski et al. 2012). Whereas the potential of oxidation-reduction of soil significantly determines participation in the form of a mobile element, which can enter the biological cycle, in relation to the total element content. Both pH and Eh are related to each other by the so-called rH factor (Clark 1923, Drobnik and Latour 2003). Its value in the studied soils was 21, which indicates slightly oxidizing conditions. Such conditions favor the occurrence of an oxidized arsenic form in soils. The As behavior in soil differs from most of the metallic elements, because of its anionic character, as expected.

Total metals concentration in non-contaminated soil and plants

According to the Polish regulation regarding acceptable metal(loid)s content for soils, the experimental soil meets the requirements for agricultural soil in terms of metal(loid)s

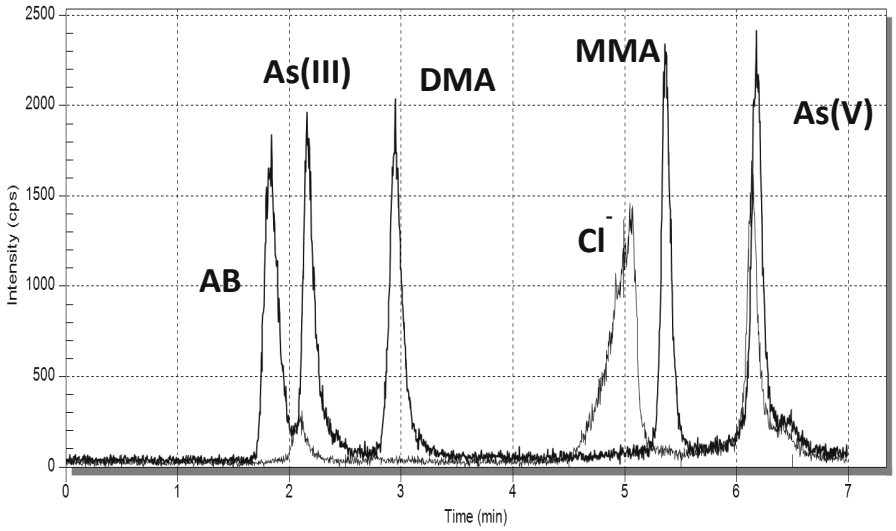

Fig. 1. An example of arsenic species chromatogram with chloride interference. AB, As(III), DMA, MMA and As(V) ions were separated with retention time: 1.84, 2.16, 2.95, 5.36, 6.17 min. respectively. Chromatographic conditions: column – Hamilton PRP-X100 (150 mm × 4.6 mm, particle size=5 µm); gradient elution – A: 20 mM NH_4NO_3 (pH=8.7), B: 60 mM NH_4NO_3 (pH=8.7)

Table 1. Validation parameters of the analytical procedure

Analyte	Limit of Detection (LOD)	Recovery [%]	RSD repeatability [%]	Uncertainty [%]
As(III)	0.08	96	2.9	12
As(V)	0.12	104	2.4	11
AB	0.16	93	3.7	17
MMA	0.08	95	3.1	12
DMA	0.09	95	2.7	11

Table 2. Basic physicochemical parameters of soils

Type of soil	pH	Eh [mV]	Conductivity [mS]
Non contaminated soil	7.1±0.5	195±5	2.71±0.13
Control soil *Melissa officinalis*	7.3±0.5	196±5	2.82±0.14
Control soil *Salvia officinalis*	7.4±0.5	192±5	2.44±0.12
As(V) contaminated soil	7.1±0.5	196±5	2.96±0.15
As(V) contaminated soil (after *Melissa officinalis* sampling)	7.4±0.5	195±5	2.81±0.14
As(V) contaminated soil (after *Salvia officinalis* sampling)	7.4±0.5	191±5	2.55±0.13
As(III) contaminated soil	7.2±0.5	193±5	2.87±0.14
As(III) contaminated soil (after *Melissa officinalis* sampling)	7.4±0.5	190±5	2.41±0.12
As(III) contaminated soil (after *Salvia officinalis* sampling)	7.3±0.5	196±5	2.78±0.14

content. The soil on which plants grew (non-contamined soil) was purchased commercially and did not contain excessive amounts of metals (Table 4). As shown in the previous studies (Szakova et al. 2018), the type of soil on which the herbaceous plants grow is very important. The obtained results indicate that peppermint (*M. x piperita*), which has grown on this soil, contained small amounts of metals and arsenic (0.16 mg·kg^{-1}), whereas compared to previous literature reports, it also contained low amounts of zinc (16.5 mg·kg^{-1}) and copper (7.49 mg·kg^{-1}). Mihaljev et al. (2014) surveyed the trace element content in 14 species of medical plants, including chamomile and peppermint. In comparison to Mihaljev et al. (2014) study, manganese concentration in chamomile (*M. recutita*) was higher and closely related to the higher content of this element in the soil (manganese concentration in control soil was 455 mg·kg^{-1}). In terms of copper, cobalt and zinc content in chamomile (*M. recutita*), compared to the previously study (Mihalijev et al. 2014), lower concentrations of these element were found, respectively Cu – 4.94, Co – 0.15 and Zn – 19.8 mg·kg^{-1}. In the case of peppermint (*M. x piperita*), the results were opposite in comparison to the data obtained by the previously mentioned authors. Higher concentrations of cobalt and nickel were found in the peppermint samples and were respectively 0.18 and 2.69 mg·kg^{-1}. The control sample of chamomile contained lower amounts of chromium, arsenic and cadmium, compared to the results obtained by Szakova et al. (2018). Pytlakowska et al. (2012) studied the total content of elements in herbs, including lemon balm (*M. officinalis*) and sage (*S. officinalis*). In these herbs samples there was more zinc and less copper and manganese.

Total As contents in soil and plants

The soil used for the plant growth was contaminated with 2 g·L^{-1} of As(III) and As(V) solutions. However, as the study showed, the concentration of this element in soil was higher than expected (on average approx. 200 mg·kg^{-1}). This may have been caused by the errors during the analysis, the inhomogeneity of the soil or soil contamination from the air in the form of dust fall. The composition of the Silesian PM2.5 is due to the high use of fossil fuels for energy production and the concentration of industry in the region (big cokeries, steelworks, and non-ferrous metal smelters). The relatively high concentrations of As in Zabrze and Katowice fit this argumentation very well (Rogula-Kozłowska et al. 2013). According to the air state studies in Silesia (Poland), arsenic concentration in the dust in Zabrze and Katowice is high and the sum of thirteen fractions of arsenic in dust was even 2.54 ng·m^{-3} (Rogula-Kozłowska et al. 2015).

Chemical composition of non-contaminated soil and plants are shown in Table 4. Non-contaminated soil contained 36.3 mg·kg^{-1} of arsenic and 11.0 mg·kg^{-1} of lead, 22.9 mg·kg^{-1} of zinc or 3.58 mg·kg^{-1} of chromium. Table 5 shows the result of the total arsenic determination in the contaminated soil, plants samples growing on the contaminated substrate, commercially purchased herbs (fix) and reference material NIST Tomato Leaves 1573a. Preliminary results of the total arsenic in plants growing on polluted substrate showed that arsenic is the most commonly accumulated from the substrate by *M. x piperita*. The highest concentration of arsenic from plants growing on polluted substrate showed *M. x piperita*, which most easily accumulated this element from the substrate. The second in order was *S. officinalis*, followed by *M. officinalis* and *M. recutita.* Higher total arsenic concentrations in the studied plants occurred when they were grown on a substrate enriched with As(V).

Even herbs in which the leaves contained predominantly As(V) grew on soil contaminated with a reduced form of arsenic. In the roots of herbs growing on As(III) contaminated soils, the share of the reduced arsenic form was greater (Table 3). Table 4 presents physicochemical soils conditions and Table 5 shows the total arsenic content in soil as well as in plants growing on them. There is no significant correlation relationship between pH and the total arsenic content in soil, taking into account the species of studied herbs ($R^2_{M.\ officinalis}$=0.319; $R^2_{S.\ officinalis}$=0.318). In addition, the analysis of the obtained research results allowed finding a significant correlations between soil pH and the presence of various arsenic species in plants. The content of As(V) and MMA in plant roots strongly correlated with pH, for example: R^2 As(V)$_{M.\ officinalis}$=0.822 and R^2 As(V)$_{S.\ officinalis}$=0.971 or R^2 As(V)$_{M.\ officinalis}$=0.822 and R^2 As(V)$_{S.\ officinalis}$=0.971. No such strong correlations were found between pH and other arsenic forms.

Table 3. Concentration of arsenic species in studied plants

Analyte	Non-contaminated soil [mg·kg^{-1}]	Acceptable metal(loid)s content for agricultural soils*	*Matricaria recutita (L.) Rauschert* [mg·kg^{-1}]	*Mentha x piperita* [mg·kg^{-1}]	*Melissa officinalis L.* [mg·kg^{-1}]	*Salvia officinalis L.* [mg·kg^{-1}]
Mn	455±95	–	130.7±27.4	55.7±11.7	82.7±17.2	92.0±19.3
Co	5.01±0.15	30	0.15±0.02	0.18±0.02	0.19±0.02	0.24±0.02
Ni	5.04±0.50	150	0.36±0.04	2.69±0.27	1.65±0.17	0.94±0.09
Cu	7.51±0.93	150	4.94±0.61	7.49±0.92	5.35±0.66	5.02±0.62
Zn	22.9±8.0	500	19.8±6.9	16.5±5.8	16.7±5.8	16.0±5.6
As	16.3±4.5	20	0.09±0.02	0.16±0.04	0.17±0.04	0.17±0.04
Cd	0.24±0.02	3	0.53±0.06	0.20±0.02	0.15±0.02	0.04±0.01
Pb	11.0±3.1	250	0.45±0.13	0.94±0.26	1.32±0.37	1.51±0.42
Cr	3.58±0.41	300	0.98±0.11	1.13±0.13	1.53±0.18	1.95±0.22
Ba	61.8±10.5	400	23.3±3.9	46.6±7.9	35.9±6.1	54.5±9.3
Ag	0.28±0.04	–	0.06±0.01	0.16±0.02	0.11±0.02	0.06±0.01

* – values established by Polish legislation (Dz.U. 2016)

Table 4. Chemical composition non-contaminated soil and control plants (growing on non-contaminated soil)

Soil	Arsenic* [mg·kg^{-1}]
Non-contaminated soil	36.3±10.1
Soil contaminated with As(III)	259±72
Soil contaminated with As(III) on which *Salvia officinalis L.* grows	356±99
Soil contaminated with As(III) on which *Melissa officinalis L.* grows	294±82
Soil contaminated with As(V)	326±91
Soil contaminated with As(V) on which *Salvia officinalis L.* grows	325±90
Soil contaminated with As(V) on which *Melissa officinalis L.* grows	363±101
Plant	**Arsenic [µg·kg^{-1}]**
Matricaria recutita (L.) Rauschert fix	1.08±0.30
Matricaria recutita (L.) Rauschert control plant	3.09±0.86
Matricaria recutita (L.) Rauschert (soil contaminated with As(III))	17.3±4.8
Matricaria recutita (L.) Rauschert (soil contaminated with As(V))	20.6±5.7
Mentha x piperita fix	1.90±0.53
Mentha x piperita control plant	24.0±6.7
Mentha x piperita (soil contaminated with As(III))	166±46
Mentha x piperita (soil contaminated with As(V))	209±58
Salvia officinalis L. fix	1.94±0.54
Salvia officinalis L. control plant	2.98±0.83
Salvia officinalis L. (soil contaminated with As(III))	78.0±21.7
Salvia officinalis L. (soil contaminated with As(V))	81.9±22.8
Melissa officinalis L. fix	1.67±0.46
Melissa officinalis control plant	1.99±0.55
Melissa officinalis L. (soil contaminated with As(III))	29.2±8.1
Melissa officinalis L. (soil contaminated with As(V))	33.1±9.2
CRM NIST Tomato Leaves 1573a	114±32 Certified 112±4

fix – commercially available herbal teas purchased at the pharmacy,
control plant – plants growing on the non-contaminated soil,
* – average arsenic concentration,
N=3 – the number of repetitions of tested samples.

Table 5. Concentration of arsenic species in studied plants

Type of samples		AB [µg·kg^{-1}]	As(III) [µg·kg^{-1}]	DMA [µg·kg^{-1}]	MMA [µg·kg^{-1}]	As(V) [µg·kg^{-1}]	Sum of extracted As species [µg·kg^{-1}]
Melissa officinalis L.							
control leaf		<0.16	<0.08	<0.09	0.34±0.04	1.65±0.18	1.99±0.22
control stem		<0.16	0.37±0.04	<0.09	<0.08	1.29±0.14	1.66±0.18
fix		<0.16	0.36±0.04	<0.09	0.17±0.02	1.06±0.12	1.59±0.18
Contaminated As(III)	leaf	<0.16	9.48±1.14	6.6±0.73	3.47±0.42	9.69±1.07	29.2±3.36
	stem	1.02±0.17	10.5±1.26	3.45±0.38	3.88±0.47	8.14±0.89	27.0±3.17
Contaminated As(V)	leaf	0.69±0.12	1.29±0.16	0.99±0.11	3.69±0.44	15.6±1.72	35.3±2.55
	stem	0.49±0.08	3.74±0.45	2.31±0.25	5.09±0.61	19.8±2.18	31.4±4.29
Matricaria recutita (L.) Rauschert							
control leaf		<0.16	0.94±0.11	<0.09	0.62±0.07	1.56±0.17	3.12±0.35
control stem		<0.16	1.40±0.17	<0.09	0.56±0.07	2.17±0.24	4.13±0.48
fix		<0.16	0.13±0.02	<0.09	<0.08	0.85±0.09	0.98±0.11
Contaminated As(III)	leaf	<0.16	9.45±1.13	<0.09	0.57±0.07	8.46±0.93	17.5±2.13
	stem	<0.16	4.11±0.49	1.13±0.12	0.68±0.08	9.48±1.04	15.4±1.73
Contaminated As(V)	leaf	<0.16	4.48±0.54	0.51±0.06	2.69±0.32	12.5±1.38	20.6±2.30
	stem	<0.16	6.18±0.74	2.00±0.22	2.02±0.24	7.49±0.82	18.7±2.02
Salvia officinalis L.							
control leaf		<0.16	0.59±0.07	<0.09	0.20±0.02	1.98±0.22	2.67±0.31
control stem		<0.16	0.41±0.05	<0.09	<0.08	2.06±0.22	2.66±0.27
fix		<0.16	1.06±0.13	<0.09	0.51±0.06	2.36±0.26	3.92±0.45
Contaminated As(III)	leaf	4.80±0.82	20.5±2.46	9.94±1.09	18.4±2.21	25.4±2.80	78.9±9.38
	stem	13.0±2.21	50.9±6.11	<0.09	32.7±3.92	19.0±2.09	116±14.33
Contaminated As(V)	leaf	<0.16	20.9±2.51	10.0±1.10	24.5±2.94	30.3±3.33	85.6±9.88
	stem	9.45±1.61	5.00±0.60	5.44±0.60	25.3±3.04	56.5±6.22	102±12.1
Mentha x piperita							
control leaf		2.48±0.42	3.37±0.40	<0.09	1.99±0.24	7.04±0.77	14.9±1.83
control stem		1.52±0.26	3.05±0.37	<0.09	1.24±0.15	4.41±0.49	10.2±1.27
fix		<0.16	0.56±0.07	<0.09	0.31±0.04	2.31±0.25	3.18±0.36
Contaminated As(III)	leaf	20.1±3.42	41.4±4.97	<0.09	32.1±3.85	54.9±6.04	148±18.3
	stem	13.7±2.33	69.9±8.39	<0.09	58.7±7.04	36.7±4.04	179±21.8
Contaminated As(V)	leaf	24.4±4.15	64.8±7.78	9.87±1.09	36.4±4.34	89.5±9.84	225±27.2
	stem	19.7±3.35	44.9±5.39	<0.09	35.6±4.27	125±13.8	245±26.8

control leaf – leaves of plant grown on non-contaminated soil,
control stem – stems of plant grown on non-contaminated soil,
fix – sample of commercially purchased plant.

Sequential chemical extraction of soils

Information on the forms of heavy metals and metalloids occurrence in soil and the mechanisms of their binding to organic and inorganic components of soil are very important, and the same knowledge of only the total content of elements in soil is insufficient. By examining the concentration of heavy metals and their chemical form, the conditions prevailing in the soil need to be taken into account, especially the physical and chemical properties, which significantly affect the mobility of trace elements and their absorption by plants (Fijałkowski et al. 2012). The soil extracts were subjected to the quantitative analysis with an ICP-MS spectrometer. Table 6 shows the results of the sequential chemical extraction performed according to Tessier method (Tessier et al. 1979). The fractionation showed

that arsenic contained in the soil contaminated with various As species was mainly related to the oxide and organic-sulfide fractions. The highest arsenic percentage occurred in the oxide fraction for the soils polluted with As(V) and amounted to nearly 60%. In the unpolluted soil, arsenic occurred mainly in the conditionally non-mobile fraction associated with organic matter (F4 – Oxidisable fraction). Table 6 clearly shows an almost double predominance of the percentage share of arsenic associated in this fraction with organic matter. In this fraction elements are tightly bound to the soil matrix, but as a result of environmental changes and natural soil mineralization, under appropriate conditions (low pH, changes in the oxidation and reduction potential) they can complement soluble and exchangeable forms and may be released into the aqueous phase. Under conditions favoring oxidation the metals associated with the organic form may also be available to plants. Soil contamination by significant amount of arsenic caused this element to occur in the soil in the oxide fraction and was bound to iron and manganese oxides (Mizerna and Król 2018). Sequential chemical extraction of the studied soils clearly showed that strong arsenic soil contamination results in an increase in the presence of this element in more mobile fraction.

Arsenic species in plant samples

Table 5 shows total arsenic contents in the digested plants, whereas Table 6 presents the speciation analysis results for the plant sample extracts. Among the examined plants growing on the contaminated substrate, peppermint (*M. x piperita*) demonstrated the highest total arsenic concentration. Sage (*S. officinalis*) was the second in its "readiness", followed by lemon balm (*M. officinalis*) and chamomile (*M. recutita*). The results also showed that the studied herbaceous plants absorbed the oxidized arsenic form from the substrate more readily. The oxidized arsenic form has a greater ability to accumulate in the herbaceous plants. It may be caused by the biochemical similarity between arsenates and phosphate groups in the aerobic phosphorylation. The phosphate groups are always involved in the formation of many functional biological plant molecules. During these biological processes, arsenates can be "treated by the plant" as phosphate groups (Yuan et al. 2007). As a result, the plant treats arsenates as phosphates and joins metabolic processes, including respiratory processes, which negatively affects their growth and development. The results confirm those of previous studies by Szakova et al. (2011), which showed that *Mentha aquatica* could be a promising herbal plant to be tested as a potential phytoremediation plant for the arsenic-contaminated soils. The authors investigated the content of arsenic species in the *M. aquatica* growing in polluted areas and found out that As(V) (and to lesser extent DMA and MMA) was the predominant arsenic form. Figures 2abcd show the percentage of the arsenic species in the investigated herbs. Lemon balm (*M. officinalis*) showed that both the control sample (stems and leaves) and commercially purchased fix tea were dominated by the oxidized arsenic form. Among the arsenic organic species, low MMA amounts were present only in the control sample leaves and fix tea. When the plant grew on the As(III)-contaminated soil, the As(III) amount in the lemon balm (*M. officinalis*) leaves, and especially in its stems, increased significantly. In addition, these samples also contained organic arsenic species such as AB, MMA and DMA. In the control lemon balm (*M. officinalis*) samples, AB and DMA were not found. The appearance of these arsenic species was most likely related to the changes taking place in the plant which metabolized As(III). One of the visible effects was the presence of methylated arsenic species. When lemon balm (*M. officinalis*) was grown on the soil enriched with As(V), the ion content in the plant visibly increased. In addition, the AB, MMA and DMA concentrations were also present. Interestingly, As(III) was not found in the control sample of the lemon balm (*M. officinalis*) leaves. Only a small amount of As(III) appeared in the leaves of lemon balm (*M. officinalis*) growing on the soil contaminated with the oxidized arsenic form. The situation could be correlated with the redox potential, which was 194.8 mV in the As(V)-polluted soil. Under these conditions, the Clark coefficient (rH=(Eh+(0.06·pH))/0.03) is

Table 6. Results of total arsenic concentration in soil samples after sequential chemical extraction (Tessier et al. 1979) [mg·kg^{-1}] and percentage of individual fractions [%]

Type of soil	Fraction					
	F0	F1	F2	F3	F4	F5
Non-contaminated soil	0.03 (0.1%)	0.09 (0.1%)	4.50 (6.6%)	19.8 (28.9%)	42.7 (62.5%)	1.26 (1.8%)
Non-contaminated control soil on which *S. officinalis* grows	0.03 (0.1%)	0.11 (0.2%)	4.89 (9.3%)	17.0 (32.3%)	28.8 (54.7%)	1.86 (3.5%)
Soil contaminated with As(III)	6.48 (0.8%)	19.6 (2.5%)	99.1 (12.8%)	350 (45.2%)	292 (37.8%)	6.75 (0.9%)
Soil contaminated with As(III) on which *S. officinalis* grows	3.28 (0.4%)	10.6 (1.3%)	62.2 (7.8%)	458 (57.7%)	251 (31.6%)	8.86 (1.1%)
Soil contaminated with As(V)	6.34 (0.8%)	17.4 (2.1%)	107 (12.8%)	438 (52.0%)	265 (31.5%)	7.68 (0.9%)
Soil contaminated with As(V) on which *S. officinalis* grows	4.34 (0.5%)	14.8 (1.7%)	82.0 (9.2%)	520 (58.2%)	262 (29.3%)	10.4 (1.2%)

Fraction: F0 – Water-soluble metal fraction, F1 – Exchangeable, F2 – Acido-soluble, F3 – Reducible, F4 – Oxidisable, F5 – Residual

21 which indicates oxidation conditions (Clark 1923, Drobnik and Latour 2003). In oxidative conditions, the oxidized arsenic species is the more frequently occurring form. The oxidized inorganic arsenic form and MMA dominated in both the leaves and stems of lemon balm (*M. officinalis*) growing on the soil rich in As(V).

For chamomile (*M. recutita*), As(V) dominated in the stem and leaf control samples. However, approx. 20% of the reduced arsenic form content and a small MMA amount appeared in the leaves. The stems contained only As(V) and MMA. The herbal chamomile fix tea bought at the shop contained only As(V) and small As(III) amounts. The toxic As(III) exceeded the As(V) amount in the chamomile (*M. recutita*) leaves which grew on the As(III)-contaminated soil. The methyl arsenic species (MMA and DMA) appeared in the chamomile (*M. recutita*) stem, most likely due to the metabolic changes. At the same time, the oxidized (and less toxic) arsenic form concentration increased. The oxidized arsenic form was dominant in the chamomile (*M. recutita*) samples growing on the As(V)-contaminated soil. Nonetheless, other species were also determined. The As(V) concentrations in the stems and leaves were 12.5 and 7.49 $\mu g \cdot kg^{-1}$, respectively.

Sage (*S. officinalis*) contained mainly As(V) and small amounts of MMA and As(III) (leaves) in the control samples. Similar concentrations and contents of the arsenic ionic forms were found in sage (*S. officinalis*) purchased commercially as fix tea. A very interesting distribution of various arsenic ionic forms concentrations occurred in the sage (*S. officinalis*) samples growing on the As(III)-polluted soil. Significant amounts of the reduced inorganic and organic (including AB) arsenic forms appeared in the sage (*S. officinalis*) leaves. The contents of As(III) and As(V) were comparable. In the stems, the As(III) concentration was higher than those of As(V) and MMA. Probably, the plant did not cope with such strong As(III) soil contamination, whose additional effect was showed by stunted plants with a strongly reduced form. Sage (*S. officinalis*) reacted better to the As(V) soil pollution by converting As(V) into the methyl species. Importantly, the highest As(V) percentage was determined in this plant.

The control peppermint (*M. x piperita*) samples contained mostly As(V). However, they also consisted of AB, MMA, or As(III). Nonetheless, the commercially purchased peppermint tea contained only As(V) and organic arsenic species. When compared to other herbaceous plants tested in this experiment, the control peppermint (*M. x piperita*) samples contained the highest arsenic contents. For plants growing on the As(V)-polluted soils, the As(V) concentrations in leaves and stems were 89.5 and 125 $\mu g \cdot kg^{-1}$, respectively. The samples also consisted of organic arsenic compounds and As(III). Although the herb was grown on a medium rich in As(V), significant amounts of toxic As(III) were found in its tissues. Peppermint (*M. x piperita*) growing on the soils polluted with As(III) contained its largest amounts exceeding the oxidized arsenic content. In comparison with the remaining plants, peppermint (*M. x piperita*) demonstrated the highest degree of the contamination absorption from the soil. The

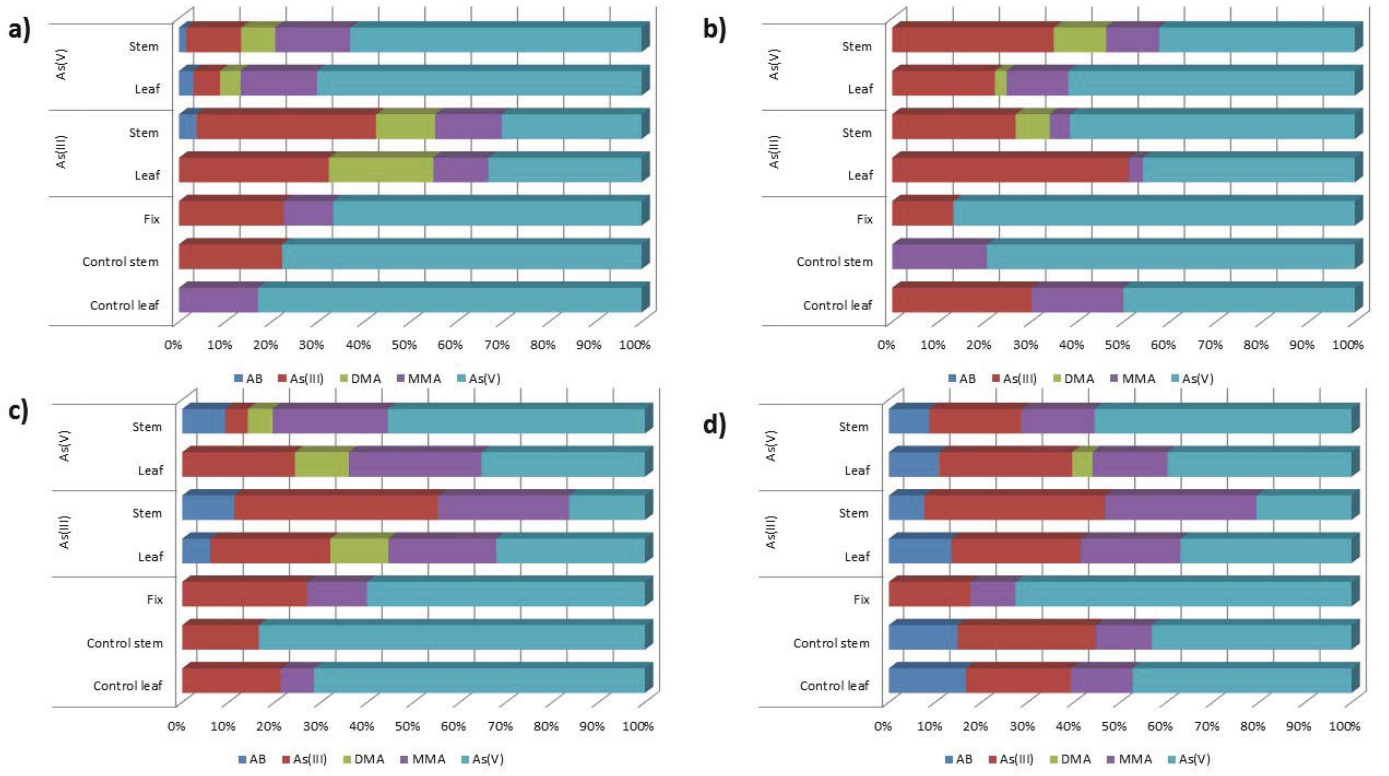

Fig. 2. Percentage share of arsenic species in: a – *Melissa officinalis L.*, b – *Matricaria recutita (L.) Rauschert*, c – *Salvia officinalis L.*, d – *Mentha x piperita*; control leaf – sample of plant leaves growing on the non-contaminated soil; control stem – sample of plant stems growing on the non-contaminated soil; fix – sample of commercially purchased herb in the form of sachets for brewing; As(III) – a sample of a plant grown on contaminated with As(III) soil; As(V) – a sample of a plant grown on soil contaminated with As(V)

research confirmed the results obtained by Szakova et al. (2009), who studied the *M. aquatica* growing in areas contaminated with arsenic. They found out that its content in the above-ground plant parts occurred in the following order: As(V)>As(III)>>DMA>MA.

The results of commercially tested herbs showed a low total arsenic content, lower than the herbs grown in the pot experiment. The total arsenic concentrations were respectively: *M. officinalis L.*– 1.67 $\mu g \cdot kg^{-1}$, *M. recutita* – 1.08 $\mu g \cdot kg^{-1}$, *S. officinalis* – 1.94 $\mu g \cdot kg^{-1}$ and *M. x piperita* – 1.90 $\mu g \cdot kg^{-1}$. Speciation analysis showed also that in these samples the oxidized arsenic form dominate. However, small amounts of As(III) (*S. officinalis L.* – 1.06 $\mu g \cdot kg^{-1}$, *M. x piperita* – 0.56 $\mu g \cdot kg^{-1}$) or MMA (*S. officinalis L.* – 0.51 $\mu g \cdot kg^{-1}$, *M. x piperita* – 0.31 $\mu g \cdot kg^{-1}$) were found.

Arsenic phytoaccumulation coefficient

The obtained results helped to determine the phytoaccumulation coefficient of the studied herbaceous plants. The obtained results indicate that for chamomile (*M. recutita*) there is a poor degree of phytoaccumulation ($WF_{As(III)}$=0.07, $WF_{As(V)}$=0.06). In contrast, lemon balm (*Melissa officinalis*) ($WF_{As(III)}$=0.11, $WF_{As(V)}$=0.10) and sage (*S. officinalis*) ($WF_{As(III)}$=0.30, $WF_{As(V)}$=0.25) demonstrated an average degree of phytoaccumulation. The highest degree of arsenic accumulation was found for peppermint (*M. x piperita*) ($WF_{As(III)}$=0.64, $WF_{As(V)}$=0.64). Peppermint (*M. x piperita*) was also studied by Łaszewska et al. (2007). However, they studied specific accumulation coefficients for metals such as cadmium, chromium, nickel, lead, copper, zinc, manganese or iron but did not investigate arsenic. The peppermint (*M. x piperita*) leaves accumulated manganese, nickel and lead intensively while its roots and flowers accumulated nickel and lead. All the morphological peppermint (*M. x piperita*) parts demonstrated a high arsenic phytoaccumulation coefficient value.

Conclusions

Among the studied plants growing on the polluted soils, peppermint (*M. x piperita*) demonstrated the highest arsenic concentration. It most easily accumulated the discussed element from the substrate. Sage (*Salvia officinalis L.*) was the second in order, followed by lemon balm (*Melissa officinalis L.*) and chamomile (*M. recutita*). The sequential chemical extraction showed that arsenic in the soil contaminated with its various species was mainly bound to the oxide and organic--sulfide fractions. The results also revealed that the oxidized arsenic form was more readily absorbed from the substrate by the studied herbaceous plants. The oxidized arsenic form had a greater ability to accumulate in herbaceous plants. The plant response to strong environmental pollution varied and depended on their type and arsenic species with which the soil was contaminated. In most cases, the contamination of the soil on which the plants grew resulted in the appearance of organic arsenic compounds (most often MMA). The obtained results indicate that the phytoaccumulation degree was low (WF≤0.01) for chamomile (*M. recutita*). In contrast, lemon balm (*M. officinalis*), peppermint (*M. x piperita*) and sage (*S. officinalis*) manifested an average phytoaccumulation degree, with the highest value of the arsenic accumulation for peppermint (WF≤1.0). *Mentha x piperita* could be a promising herbal plant to be tested as a potential phytoremediation plant for the arsenic-contaminated soils. The study provided important information on the contents of organic and inorganic arsenic species in selected herbaceous plants, which often constitute the components of dietary supplements, including the most popular herbal teas.

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Mobilność arsenu i jego form jonowych w wybranych ziołach

Streszczenie: Celem badań było sprawdzenie tolerancji rumianku (*Matricaria recutita (L.) Rauschert*), mięty pieprzowej (*Mentha x piperita*), melisy lekarskiej (*Melissa officinalis L.*) i szałwii (*Salvia officinalis L.*) na zwiększoną zawartość nieorganicznych form jonowych arsenu w glebie. Zdolność ziół do akumulacji arsenu została przetestowana w doświadczeniu wazonowym, w którym gleby były zanieczyszczone przez As(III) lub As(V). Formy specjacyjne arsenu: As(III), As(V), AB (arsenobetaina), MMA (kwas monometylowy) i DMA (kwas dimetylowy) rozdzielono na kolumnie Hamilton PRP-X100 za pomocą wysokosprawnej chromatografii cieczowej połączonej ze spektrometrią mas z plazmą wzbudzoną indukcyjnie (HPLC-ICP-MS). W pracy zbadano zawartość arsenu w glebie i ziołach, a także mobilność form arsenu z gleby do badanych roślin zielnych. Mięta charakteryzowała się największym stopniem fitoakumulacji i stężenia arsenu wśród badanych roślin. Sekwencyjna ekstrakcja chemiczna wykazała, że arsen w zanieczyszczonej glebie był głównie związany z frakcjami tlenkowymi i siarczkowo-organicznymi. Wyniki pokazały również, że utleniona forma arsenu miała większą zdolność do akumulacji w ziołach i była łatwiej absorbowana z podłoża przez badane rośliny. Badania wykazały, że odpowiedź roślin na stres arsenowy była charakterystyczna dla danego gatunku i zróżnicowana w zależności od formy arsenu, którym zanieczyszczono glebę. W większości przypadków skutkowało to pojawieniem się organicznych pochodnych arsenu.