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*Original article* ■

# Bioavailability of Heavy Metals in the Soil from Different Locations of Medicinal Herbs

Biljana Kaličanin[1], Dragan Velimirović[1], Ivana Arsić[1], Sofija Đorđević[2]

[1]*University of Niš, Faculty of Medicine, Department of Pharmacy, Serbia*
[2]*Institute for Medical Plant Research «Dr Josif Pančić», Belgrade, Serbia*

## SUMMARY

**Medicinal herbs and their mixtures, which are widely used for prevention and treatment of some disease, can also present health risks due to the presence of toxic metals such as Pb and Cd. The application of different agrotechnical practices during plant growing season, as well as the process of circulation of substances in nature, may be the cause of plant contamination.**

**The aim of this study was to determine the content of lead, cadmium and copper from soil which are bioavailable for absorption by plant, as well as the total content of these metals in some medicinal herbs that were cultivated in two different locations. The presence of these metals in the samples was detected using highly sensitive microanalytical technique potentiometric stripping analysis (PSA).**

**The mean value of lead total content in the analyzed samples of medicinal herbs *Chamimillae flos*, *Urticae folium*, *Menthae folium*, *Altheae radix* and *Basilici herba*, which were grown at the sites near the industrial zone, was about 1.55 μg/g, 1.82 μg/g, 1.90 μg/g, 1.99 μg/g and 2.74 μg/g, respectively. Contrary to this, the total content of this toxic metal in the analyzed plant samples grown on rural areas was detected only on some sites.**

**Based on the results of this study, it can be concluded that medicinal herbs contained a certain amount of lead and that its content varied depending on the location at which the plant species were grown as well as on plant affinity to certain metal. Cadmium and copper were not detected in the tested plant material.**

***Key words:*** **soil, medicinal herbs, toxic metals, bioavailability, potentiometric stripping analysis**

Corresponding author:

**Biljana Kaličanin** •
phone: +3814226644•
e-mail: bkalicanin@yahoo.com •

## INTRODUCTION

Herbal drugs and galenic forms (decocts or extracts) obtained from these natural drugs are widely consumed as home remedies and raw materials for the pharmaceutical industry. The use of medical plants in both crude and prepared forms has greatly increased, and although herbal remedies are often perceived as being natural and therefore safe, they are not free from adverse effects (1). Various reports have discussed the potential health implications of trace metals in medicinal herbs, since the herbal bush is known to accumulate them (2, 3). One of the major reasons to monitor the levels of toxic metals in medicinal plants is that the contamination of the general environment has increased. The sources of this environmental pollution are quite different, ranging from industrial and traffic emissions to the use of purification mud and agricultural expedients such as cadmium containing dung, organic mercury fungicides and the insecticide lead arsenate. Medicinal plants are normally grown in acidic soils, where lead is potentially more bioavailable for root uptake (4). The concentrations of metals in various soils are associated with biological and geochemical cycles and are influenced by anthropogenic activities, such as agricultural practices, transport, industrial activities and waste disposal. Once the metals reach the soil, their bioavailability depends on soil pH, redox potential, and rhizosphere chemistry. That in turn increases the metal content in plant species that grow in the soil. In order to determine the value of certain metal uptake by plant, bioconcentration factor (BFC) is used (5). BFC provides an index of the ability of the plant to accumulate a particular metal with respect to its concentration in the soil substrate (6). Furthermore, these plants have a large leaf area, a characteristic that is conductive to foliar deposition and uptake of lead from the atmosphere. Lead present in plants can lead to morphological and physiological disorders in the plant, which can manifest as a reduction in leaf area, reduction in the growth of plants, and have negative effects on root system development (7). Lead can enter the human body via medicinal herbs and their products. The presence of this toxic metal, even in trace amounts, poses a potential threat to human health due to its toxic and cumulative effects.

Cadmium and lead are among the most poisonous elements and they have cumulative and toxic effects. Continuous exposure to low levels of these toxic heavy metals may result in bioaccumulation and can cause a wide variety of biological effects on human beings, depending upon the level and duration of exposure (8). Human exposure to cadmium can result from food and water consumption, or accidental ingestion of soil or dust contaminated with cadmium; from inhalation of cadmium-containing particles from the ambient air; from the inhalation of cigarette smoke, which contains cadmium absorbed by the tobacco plant; or from occupations involving exposure to cadmium fumes and dust (9). Excessive Cd exposure may lead to renal, pulmonary, hepatic, skeletal, reproductive problems and cancer. Cd intoxication primarily has a negative effect on the lungs, kidneys and bones (10).

Exposure to lead can have toxic effects on the nervous system, bones, hematopoietic system, and kidneys (11). In addition, a low dietary intake of calcium and iron as well as zinc enhances the risk of exposure to lead (12). The symptoms of acute lead compound poisoning are severe gastrointestinal disorders with digestive tract damage. Signs of haematopoiesis, liver and kidney damage may also occur. Chronic lead poisoning causes anemia, as well as various nervous system disorders (13).

Copper is widely distributed in biological tissues, where it appears largely in the form of organic complexes, many of which are metalloproteins and function as enzymes. Copper enzymes are involved in a variety of metabolic reactions, such as the utilization of oxygen during cell respiration and energy utilisation. In humans, acute copper poisoning is rare and usually results from contamination of foodstuffs or beverages by copper containers or from the accidental ingestion of copper salts. Symptoms of acute copper poisoning include salivation, nausea, vomiting and diarrhoea, all of which occur probably due to the irritant effect of copper on the gastrointestinal mucosa (14).

The aim of this study was to determinate the contents of lead, cadmium and copper which are available for absorption by plant, as well as the total content of these metals in some medicinal herbs (*Chamimillae flos*, *Urticae folium*, *Menthae folium, Altheae radix*and*Basilici herba*) that were cultivated in two different locations.

## MATERIAL AND METHODS

### *Samples*

The following medicinal herbs were used as samples in this study:

- Chamomile umbel - C*hamomillae flos*-collected in May 2011;
- Nettle leaves - *Urticae folium*-collected in June, 2011;
- Mint leaves - *Menthae folium*-collected in May, 2011;
- Altea root - *Altheae radix* and-collected in September, 2011;
- Basil leaves - *Basilici herba*-collected in June, 2011.

In order to determine the influence of closeness to potential metal sources on the content of Cd, Cu and Pb, all samples of medicinal herbs were collected from two zones - industrial and rural. Samples of medicinal herbs were collected from two sites near the industrial zone of the town Šabac and from five sites of rural area around the mountain Kopaonik. Medicinal herbs that were collected from industrial zones were cultivated plants, while medicinal herbs form rural zones were wild plants.

Soils were sampled at the same locations as the medicinal herbs samples at 20 cm depth rooting zone and mixed to form composite samples from each location.

### *Sample preparation*

Procedures for medicinal herbs (15) and soil samples preparations (16) are shown in Figure 1.

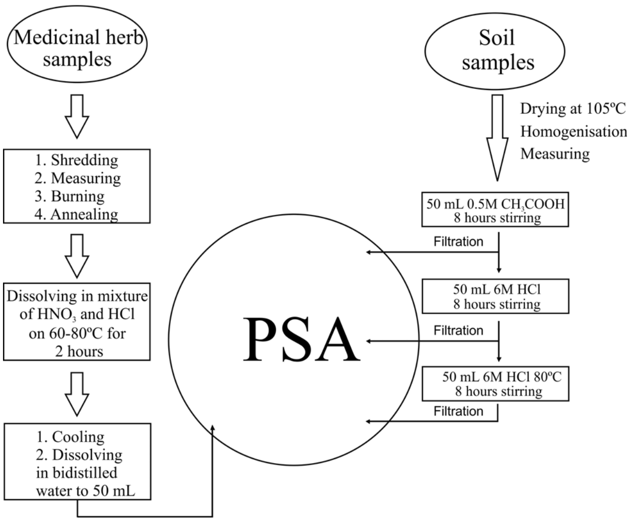



***Figure 1.*** *Medicinal herbs and soil sample preparation procedures*

### *Instrumentation*

In order to determine the contents of lead, cadmium and copper in the analysed samples of medicinal herbs and soil, a stripping analyzer M1 of domestic design and production was used (Elektrouniverzal, Leskovac and the Faculty of Technology, Novi Sad). This is a highly automatic instrument for potentiometric and chronopotentiometric stripping analysis with microprocessor control of complete process. The instrument allows the determination of all three tested elements at the same time. Experimental conditions consider the stirring rate of 4000 rpm at the electrolysis potential of-1.058eV and time of electrolysis from 300 to 600 s, depending on the element content in tested samples.

The pH values were determined using the classical method; about 4.0 g of the soils (<2 mm) were mixed with 10.0 mL deionized water in test tubes (17) and measured by Hanna instruments HI 3221 pH meter with glass HI 1131B pH electrode.

## RESULTS

All measurements were carried out in triplicate and presented as mean ± standard deviation (SD). The detected content of Pb, Cd and Cu in soil samples are shown in Table 1. Figure 2 shows the pH value of soil samples. The value of contentof lead in medicinal herbs samples of two different locations are shown in Table 2.

BFC was calculated by equation:

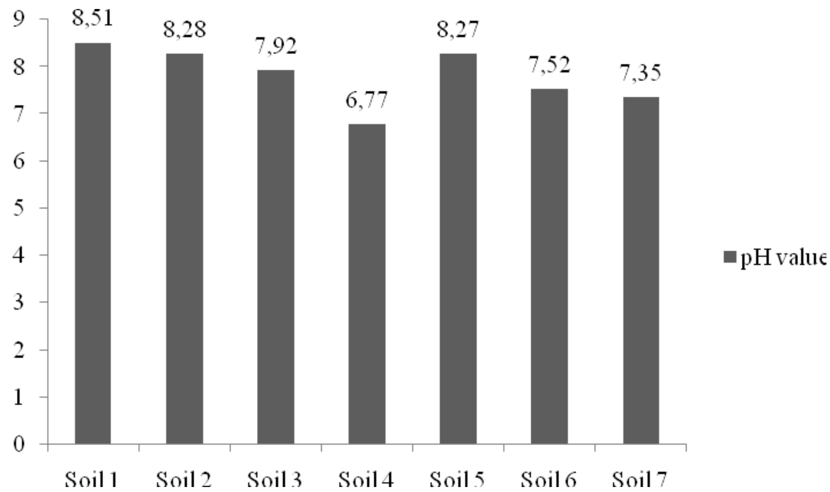
$$BFC = \frac{C(\text{metal in soil})}{C(\text{metal in plant})}$$

and presented in Table 3.

***Table 1.*** *The content of lead, cadmium and copper (μg/g±SD) in soil samples presented by fractions*

| Sample | 0.5 M $CH_3COOH$ | | 6 M HCl | | 6 M HCl (80°C) |
|---|---|---|---|---|---|
| | **Cd μg/g** | **Pb μg/g** | **Pb μg/g** | **Cu μg/g** | **Cu μg/g** |
| Soil 1 | 0.62±0.02 | 1.30±0.08 | 12.42±1.31 | 18.36±2.25 | 2.16±0.15 |
| Soil 2 | 1.14±0.11 | 2.00±0.13 | 16.79±1.63 | 134.19±4.71 | 22.54±2.85 |
| Soil 3 | 0.38±0.03 | 0.14±0.01 | 3.58±0.26 | 7.68±0.92 | 1.23±0.09 |
| Soil 4 | 0.43±0.02 | 0.15±0.01 | 4.09±0.45 | 8.29±1.11 | 1.39±0.13 |
| Soil 5 | 0.28±0.01 | 0.74±0.03 | 8.60±1.05 | 9.61±1.29 | 1.43±0.08 |
| Soil 6 | 0.42±0.02 | 0.05±0.00 | 3.38±0.23 | 8.01±1.34 | 1.55±0.15 |
| Soil 7 | 0.15±0.01 | 0.60±0.02 | 3.19±0.30 | 7.29±1.15 | 1.93±0.27 |

Soil 1, 2-industrial zones; Soil 3, 4, 5, 6, 7-rural zones




Soil 1, 2-industrial zone; Soil 3, 4, 5, 6, 7-rural zone

***Figure 2.*** *pH value of tested soil samples*

***Table 2.*** *The content (µg/g±SD) of lead in medicinal herbs samples from two different locations*

| | **Industrial zones** | | | | **Rural zones** | | |
|---|---|---|---|---|---|---|---|
| Sample | Soil 1 | Soil 2 | Soil 3 | Soil 4 | Soil 5 | Soil 6 | Soil 7 |
| *Chamomillae flos* | 1.34±0.09 | 1.76±0.10 | n.d. | 0.13±0.02 | 0.15±0.03 | n.d. | 0.07±0.01 |
| *Urticae folium* | 1.66±0.11 | 1.98±0.06 | 0.16±0.03 | n.d. | 0.05±0.00 | 0.10±0.04 | 0.12±0.04 |
| *Menthae folium* | 1.68±0.06 | 2.12±0.17 | n.d. | n.d. | n.d. | 0.08±0.02 | 0.06±0.01 |
| *Altheae radix* | 1.72±0.07 | 2.26±0.13 | n.d. | 0.09±0.01 | n.d. | n.d. | n.d. |
| *Basilici herba* | 2.52±0.14 | 2.97±0.11 | 0.04±0.01 | n.d. | 0.11±0.03 | n.d. | n.d. |

n.d. - not detected

***Table 3.*** *Bioconcentration factor (BFC) for lead in tested samples of soil and medicinal herbs*

| | **Bioconcentration factor (%)** | | | | |
|---|---|---|---|---|---|
| | *Chamomillae flos* | *Urticae folium* | *Menthae folium* | *Altheae radix* | *Basilici herba* |
| Soil 1 | 9.77 | 12.10 | 12.24 | 12.54 | 18.37 |
| Soil 2 | 9.37 | 10.54 | 11.28 | 12.02 | 15.81 |
| Soil 3 | / | 4.30 | / | / | 1.07 |
| Soil 4 | 3.07 | / | / | 2.12 | / |
| Soil 5 | 1.61 | 0.53 | / | / | 1.18 |
| Soil 6 | / | 2.91 | 2.33 | / | / |
| Soil 7 | 1.85 | 3.17 | 1.58 | / | / |

Soil 1, 2 - industrial zones; Soil 3, 4, 5, 6, 7 - rural zones

## DISCUSSION

The bioavailability of metals are generally based on the hypothesis that the free metal ion and isotopically exchangeable metal fractions (those weakly bound to soil particles) represent the pool of metal available for plant uptake (18). In order to monitor the bioavailability of heavy metals to the plants, analysis of soil was done by fractions.

Results of this study have shown that in the first fraction, under the influence of weak acidic medium (0.5M $CH_3COOH$), cadmium and lead were released from the soil. Ability of $Cd^{2+}$- and $Pb^{2+}$-ions to form a complex with $Cl^-$- and $OH^-$-ions contributes to their greater mobility and thus they become more accessible to the plants (Table 1).

Copper content in soil can be up to 20 mg/kg, but it is a poorly motile cation due to its ability to easily link to clay minerals, so it less available to the plants (19). Thus, this metal was detected in fractions where the soil had been exposed to the effects of strong acid (6M HCl) and high temperature (80 °C).

Soil pH is an important chemical property because it affects the availability of nutrients to plants and the activity of soil microorganisms. pH value for soils ranged from 6.0 to 7.5 (7). In this study, the pH value in the tested soil samples ranged from 6.7 to 8.5. Soil with slightly alkaline reaction (about 8) has a greater tendency to adsorb cations, consequently in these samples a higher content of examined metals was detected compared to soil samples with lower pH value (about 7) (Figure 2). That indicated that alkaline pH values are more adequate for greater mobility of detected metals. Besides the pH value of soil, migration of metals from soil to plant can be affected by type of soil and ionic form of specific metal. These two factors may be the reasons of greater metal mobility in alkaline soils, which was detected in this study (Table 1).

The mean values of lead total content in the analyzed samples of medicinal herbs *Chamimillae flos*, *Urticae folium*, *Menthae folium*, *Altheae radix* and *Basilici herba*, which were grown at the sites near the industrial zone, were about1.55 μg/g, 1.82 μg/g, 1.90 μg/g, 1.99 μg/g and 2.74 μg/g, respectively. The total content of this toxic metal in the samples of wild plants that originated from rural areas was detected only on some sites of these zones (Table 2). Detected content of lead in medicinal herbs from rural zones was lower compared to its content in cultivated plants from industrial zones. This indicates that closeness of industrial facilities and the main traffic roads may affect soil by increasing the concentration of some toxic metal, and thus can lead to more uptakes of these metals by plants grown on this contaminated soils.

The detected content of lead in tested samples of medicinal herbs in this study is low and under permitted limits for similar kind of plant material according to the Republic of Serbia regulations (20).

Cadmium and copper were not detected in all tested samples of medicinal herbs. The abscence of these metals in plant material may be due to lower afinity of tested medicinal herb for Cd and Cu absorption.

The permissible levels of Pb in soil worldwide ranged from 1.5 to 286 μg/g (7). There are no regulations for limits of Pb for particular medicinal herbs, because the content of this metal vary with respect to plant species, geographic region, agronomic treatment etc (7).Many authors in their studies have determined the content of metals in medicinal herbs (21-23). The content of lead in similar kinds of medicinal herbs, detected in the study of Arpadjan and al. (23), ranged from 0.19 to 8.63 μg/g, which was in accordance with the results of our study.

In this study, the content of lead detected in samples of soil was higher compared to the content of this metal, which was found in plant material. The content of Pb in analyzed medicinal herbs generally originate from the soil, but it can be said that additional contamination of plants with this metal can be due to air pollution or impact of proximity to the industrial zone, roads and the use of pesticides during their cultivation.

The value of BFC showed that medicinal herbs cultivated from industrial zones had higher BFC compared to wild plants that originate from rural zones (Table 3). That difference may occur as soil samples from industrial zones were richer in this toxic element (Table 1) and also due to considerable application of agrotechnical measures on these sites. In the group of cultivated medicinal herbs, *Basilici herba* showed the greatest tendency for Pb absorption compared to other samples of medicinal herbs which were grown in industrial zones.

## CONCLUSION

Based on results in this study, it can be concluded that lead, cadmium and copper were detected in soil samples but only lead was found in tested medicinal herbs. The content of lead in plant was lower than in soil samples. Medicinal herbs contain a certain amount of lead and that its content depends on the location at which the plant species grow. Proximity to industrial areas contributes significantly to increase of lead content in plant material. The content of lead that was detected in this study was under permitted limits, but bearing in mind its cumulative and toxic effect on human health, it is necessary to monitor and detect content of this metal in medicinal herbs.

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# BIODOSTUPNOST TEŠKIH METALA IZ ZEMLJIŠTA RAZLIČITIH LOKALITETA ZA MEDICINSKO BILJE

Biljana Kaličanin[1], Dragan Velimirović[1], Ivana Arsić[1], Sofija Đorđević[2]

[1]*Univerzitet u Nišu, Medicinski fakultet, Odsek za farmaciju, Srbija*
[2]*Institut za medicinsko istraživanje bilja «Dr Josif Pančić», Beograd, Srbija*

**Sažetak**

**Pored pozitivnog efekta koje mogu imati po ljudski organizam, pojedine lekovite biljke, kao i njihove mešavine, mogu predstavljati rizik po zdravlje usled prisustva toksičnih metala kao što su Pb i Cd. Do kontaminacije lekovitog bilja ovim metalima može doći usled primene različitih agrotehničkih mera tokom njihovog vegetacionog perioda, kao i procesom kruženja materije u prirodi.**

**Cilj ovog rada bio je određivanje i praćenje sadržaja olova, kadmijuma i bakra u zemljištu koji su biodostupni biljci za apsorpciju, kao i ukupan sadržaj ovih metala u pojedinim lekovitim biljkama koje su gajene na dve različite lokacije. Prisustvo ovih metala u ispitivanim uzorcima određeno je primenom visoko osetljive mikro-analitičke tehnike, potenciometrijske striping analize (PSA).**

**Srednja vrednost totalnog sadržaja olova u analiziranim uzorcima kamilice (*Chamimillae flos*), koprive (*Urticae folium*), nane (*Menthae folium*), belog sleza (*Altheae radix*) i bosiljka (*Basilici herba*), koji su gajeni u blizini industrijske zone, bila je oko 1,55μg/g, 1,82μg/g, 1,90μg/g, 1,99μg/g i 2,74μg/g, respektivno. Sa druge strane, totalan sadržaj Pb u uzorcima samoniklog bilja u ruralnom području, detektovan je samo na nekim lokacijma ovog područja.**

**Na osnovu rezultata u ovoj studiji, može se zaključiti da medicinsko bilje sadrži određenu količinu olova, a sadržaj ovog elementa varira u zavisnosti od lokacije na kojoj se ispitivane biljne vrste uzgajaju, kao i od njihovog afiniteta prema datom elementu. U analiziranim uzorcima medicinskog bilja kadmijum i bakar nisu detektovani.**

***Ključne reči:*** **zemljište, medicinsko bilje, toksični metali, biodostupnost, potenciometrijska striping analiza**