

## HOW MUCH SELENIUM DO MEDICINAL PLANTS CONTAIN? RESULTS OF A RESEARCH ON WILD-GROWING SPECIES FROM WESTERN ROMANIA

Diana Simona ANTAL\*, Carmen Maximiliana CANCIU\*, Cristina Adriana DEHELEAN\*, Manfred ANKE\*\*

\* University of Medicine and Pharmacy "Victor Babeș", Faculty of Pharmacy, Timișoara, Romania

\*\* Friedrich-Schiller-Universität Jena, Institut für Ernährungswissenschaften, Dornburgerstr. 24, D-07743 Jena, Germania

Corresponding author: Diana Simona Antal, "Victor Babeș" University of Medicine and Pharmacy, Faculty of Pharmacy, Department of Pharmaceutical Botany, 2 Eftimie Murgu Square, 300041 Timișoara, Romania, tel./fax: 0040256220479, e-mail: diana.antal@umft.ro

**Abstract.** The ultratrace element selenium is essential for higher animals and man. It is an active constituent of over twenty different selenoproteins from human tissues. As well, this rare nonmetal element is a potent anticarcinogen, inhibiting both chemically and virally induced tumors. The ever-increasing biological importance of Se determined us to perform the first large-scale investigation of Romanian medicinal plants in what their Se content is concerned, and to evaluate the extraction ratio of this element during decoction. ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) analysis revealed average Se contents of 43 µg/kg dry matter. The highest Se content was found in aerial parts (average of 60 µg/kg), followed by leaves (58), roots (54), flowers (35) and fruits (12). Species grown on limestone weathering soils are significantly richer in Se than the ones grown on granite or phyllite. Outstanding Se contents were measured for samples of *Betula pendula* leaves – 381, 131 and 113 µg Se/kg, *Agrimonia eupatoria* herb - 332 µg/kg, and *Galium verum* herb – 287 µg/kg. The extraction ratio of Se through decoction ranges from 4% (valerian roots) to 83% (chicory roots). The Se content and the high amounts of flavonoids in birch, agrimony and yellow bedstraw underline the value of these plants in the auxiliary treatment of various free-radical mediated diseases.

**Keywords:** selenium, medicinal plants, ICP-MS, aqueous extraction

### INTRODUCTION

Although at first only known for its toxicity, researches of the last five decades pointed to the essentiality of Se for humans and animals. In this period, a profound change of perspective on the importance of Se could be observed in medicine, agriculture, biology and nutrition. Hence, the purely toxic element Se became the essential element Se; the carcinogenic element Se turned into the ultratrace element which protects against cancer; the undesirable element Se became the ingredient of food supplements recommended in pharmacies or added to feed for domestic and wild animals. This change in perspective was triggered by the research of Schwarz and Foltz [24], who demonstrated the essentiality of Se for rat. Later studies underlined the multiple metabolic implications of Se. Today, this element is considered both toxic and essential, depending on the quantities it occurs in.

Selenium has a low abundance in the outer Earth's crust (only 0.8 mg/kg), occupying the 70<sup>th</sup> place in the list of frequency of the 98 elements it contains [23]. Its occurrence is thus similar to the one of other rare elements like iodine or gold. Although Se is ubiquitous, its distribution is uneven [14], with concentrations in soils ranging from 0.1 mg/kg in Se-deficient areas (China, Finland) to over 4.3 mg/kg in seleniferous areas (Venezuela, Ireland, parts of the USA). Cultivated surface soils have on average a lower concentration of 0.5 mg/kg. The total Se content in soils does not indicate its bioavailability. In acid soils Se is bound as ferric selenite of very low solubility and has a low availability to plants. In alkaline soils Se occurs as soluble selenate with a higher phytoavailability [10].

The essentiality of Se to the fauna and humans is due to its presence in at least twenty-five proteins and enzymatic systems, where it is incorporated as selenocysteine at the active site [8]. The uptake of Se in humans is subjected to a genetic control. Among Se containing enzymes, of special importance are

glutathione peroxidases which reduce the accumulation of peroxides and hydroperoxides, as well as deiodinases which intervene in the metabolism of thyroid hormones [13]. Selenoprotein P, the major plasma selenoprotein, defends the organism against oxidative injuries and plays a part in the detoxification of mercury [17]. Selenoprotein W plays a role in the health of cardiac and skeletal muscle [22]; selenoprotein 15 has a chemopreventive role [12]. Selenoprotein R acts as a stereospecific methionine sulfoxide reductase [16], while selenoprotein N functions catalytically in redox-processes involving thiols as electron donors [18]. A low Se status has been linked to a variety of diseases: fatal cardiomyopathy (Keshan disease), muscular dystrophy, inflammatory-degenerative deterioration of articulations (Kashin-Beck disease), cancer, immune system deficiencies, and decline in the thyroid function [2, 3]. Clinical applications of Se supplementation include a variety of acute diseases or chronic conditions associated with increased oxygen radical production (septicemia, acute pancreatitis, chronic lymphedema, endemic hemorrhagic fever, autoimmune thyroiditis) [7, 26], AIDS, cancer (lung, gastric, intestinal, prostate, breast) as well as cardiovascular and rheumatic diseases [19, 21].

Concerning the daily requirement for humans, the World Health Organization [29] established that the basal requirement is 20 µg Se/day (the intake needed to prevent pathologically relevant and clinically detectable signs of impaired function). The normative intake (serving to maintain a desirable level of tissue storage) was estimated to be 40 µg Se/day. In the USA, the Dietary Reference Intake was evaluated at 55 µg Se/day [20].

High Se levels are known to be toxic. The tolerable upper intake level, representing the highest level of daily Se intake that poses no risk or adverse effects to almost all individuals in the general population was set at 400 µg Se/day, corresponding to one-half of the no-observed-Adverse-Effect-Level of 800 µg Se/day [20].

The broad spectrum of selenium's biological implications determined us to examine its contents in the main medicinal plants used in Romanian phytomedicine, and growing wild in the Western part of the country (Banat region, Aninei Mountains). To our knowledge, this is the first large-scale investigation of the Se content in Romanian plants; 56 species were analyzed. The research had several objectives: to explore the potential contribution of medicinal plants to the Se intake, to assess the Se-status of the flora, and to point out species prone to the accumulation of this element. As medicinal plants are used in Romanian phytotherapy mainly as aqueous extracts, we determined as well to the proportion of Se passage into herbal decoctions.

## MATERIALS AND METHODS

**Plant material.** Plant samples pertaining to 56 species employed in phytotherapy were collected from various areas of the Aninei Mountains (Banat region, Romania) believed to be unpolluted (far away from roads, kilometers outside villages or towns). Samples originated from soils with different geologic origin: limestone, granite and phyllite. The naming of sites where plant samples were collected was done according to [25]. Identification of plants was carried out by Dr. D.S. Antal from the department of Pharmaceutical Botany, University of Medicine and Pharmacy Timisoara; voucher specimens were deposited in the Herbarium of the Faculty of Pharmacy. After collection,

the samples were dried at ambient temperature and deposited in cotton sacks. Previous to the determination of Se content, plants were brought to powder consistency using non-metallic devices. Dry mass at 105°C was determined for each plant product through heating during two hours in an oven (WTB Binder, Tuttlingen, Germany).

**Method of analysis.** The assessment of the Se content in was performed by inductively coupled plasma - mass spectrometry (ICP-MS). The apparatus used for this research was ThermoElemental X Series ICP-MS (Thermo Electron, Dreiech, Germany). The parameters of the measurement were detailed previously [5]. As a first step, a semi-quantitative analysis was performed, allowing the estimation of the concentration ranges in the digestion solutions of the plant materials. The quantitative determinations were carried based on a calibration curve ( $r^2 = 0.9999$ ) established with ICP Multi Element Standard Solution XXI CertiPUR Merck, diluted to obtain optimal measurement range (between 0.05 – 10.00 µg Se/l). Internal standard was rhodium. The limit of detection for Se was 0.8 µg/l.

**Accuracy of the data** was verified by a parallel analysis of two certified reference materials: Peach Leaves 1547 and Oriental Tobacco Leaves CTA-OTL-1. The agreement between the concentration indicated by the producer and the one obtained experimentally within the present study certifies the fact that mineralization and determination procedures were carried out quantitatively and correctly (Table 1).

**Table 1.** Results of selenium determination through ICP-MS in certified reference materials.

Peach Leaves 1547		Oriental Tobacco Leaves CTA-OTL-1	
Certified value (µg Se/kg)	Measured value (µg Se/kg)	Certified value (µg Se/kg)	Measured value (µg Se/kg)
120 ± 9	123	153 ± 18	145

**Sample preparation.** Weighed samples of 0.3-0.4 g dried plant material were placed in Teflon crucibles and 4 ml of nitric acid (Merck, additionally purified by subboiling), 0.25 ml hydrochloric acid (Merck, ultrapur) and 1 ml hydrogen peroxide (Merck, ultrapur) were added. Mineralization was performed in a closed system with the use of microwave energy (oven MARS 5, CEM GmbH, Kamp-Lintfort Germany), at 180°C and 11 bar pressure, for 20 minutes. The digestion solutions were transferred into volumetric flasks and made-up to 15 ml with water (nanopure); 1 ml of each solution was diluted 1:10 and analyzed by ICP-MS.

**Preparation of the aqueous extract.** In order to evaluate the proportion in which Se passes into solution, we prepared decoctions out of 17 plants, obtained as follows: 50 ml bidistilled water were added to 2.000 g dried herbal part, and heated to boiling; the temperature of 100°C was maintained for 15 minutes. After cooling and filtration, 5 ml extract were introduced in a Teflon crucible, and treated with 3 ml nitric acid subboiled and 0.250 ml hydrochloric acid ultrapur. The solution was microwave-digested, brought to 10 ml, and analyzed by ICP-MS.

**Statistic analysis** was performed by Windows 2003 Excel, using the functions for the calculation standard deviation, t-test and Pearson's coefficient (r).

## RESULTS

The investigation of the Se content by ICP-MS revealed that all analyzed samples contained this trace element (Table 2). The measured concentrations ranged from 1 µg /kg dry mass (comfrey roots, centaury herb, dyer's greenwood herb), to 381 mg/kg (birch leaves). The variation intervals for the distribution of this elements' content were as follows:

- between 1-10 µg/kg dry mass (DM): 36.0 % of samples
- between 10-50 µg/kg DM: 32.0 %
- between 50-100 µg/kg DM: 10.4 %
- between 100-200 µg/kg DM: 14.4 %
- between 200-300 µg/kg DM: 4.8 %
- between 300-400 µg/kg DM: 2.4 %

The Se content showed a variation span of three orders of magnitude – both among different species as well as within the same plant organ when collected from various sites (for example wild thyme, Table 2). Over two thirds of the samples (68%) contained less than 50 µg Se/kg. Consistently high Se levels were recorded for birch leaves, where 3 of 4 samples contained more than 100µg Se/kg. The average content of the investigated elements proved to be 43µg/kg DM.

**Table 2.** The selenium content of aerial parts (herbs) of medicinal plants ( $\mu\text{g}/\text{kg}$  dry plant).

Species	Collection site; geologic substrate	Se ( $\mu\text{g}/\text{kg}$ )	Species	Collection site; geologic substrate	Se ( $\mu\text{g}/\text{kg}$ )
<i>Agrimonia eupatoria</i>	Lisvar Hill ; C	332	<i>Lycopus europaeus</i>	Poneasca Mount.;G	7
<i>Agrimonia eupatoria</i>	Cioplăia Hill; C	61	<i>Lysimachia nummularia</i>	Steierdorf; C	3
<i>Anthyllis vulneraria</i>	Iabalcea; C	59	<i>Lythrum salicaria</i>	Lișcovu; F	218
<i>Artemisia absinthium</i>	Steierdorf; C	29	<i>Lythrum salicaria</i>	Poneasca mead.;G	5
<i>Artemisia absinthium</i>	Păuleasca; C	30	<i>Melilotus officinalis</i>	Caraș mead.; C	85
<i>Centaurium erythraea</i>	Tâlva Zânei; C	1	<i>Mentha longifolia</i>	Lisovacea; C	3
<i>Chelidonium majus</i>	Lăpușnic valley; C	6	<i>Mentha pulegium</i>	Steierdorf; C	16
<i>Chelidonium majus</i>	Gârliște; C	12	<i>Origanum vulgare</i>	Baciului Valley; C	89
<i>Cichorium intybus</i>	to Doman; C	64	<i>Origanum vulgare</i>	Secu lake; F	14
<i>Cichorium intybus</i>	Lisovacea; C	27	<i>Origanum vulgare</i>	Livada Mare; C	1
<i>Echium vulgare</i>	Carașova; C	12	<i>Origanum vulgare</i>	Mărghitaș; C	31
<i>Epilobium parviflorum</i>	Steierdorf; C	237	<i>Origanum vulgare</i>	Poiana Scocu; C	96
<i>Epilobium parviflorum</i>	Goseni; F	13	<i>Potentilla anserina</i>	Golumbu; C	50
<i>Epilobium parviflorum</i>	Anina; C	24	<i>Solidago virgaurea</i>	Bido Valley; C	119
<i>Equisetum arvense</i>	Scocu; C	129	<i>Taraxacum officinale</i>	Steierdorf; C	188
<i>Equisetum arvense</i>	Crainic mead.; F	30	<i>Taraxacum officinale</i>	Lisovacea; C	45
<i>Equisetum arvense</i>	Poneasca Mount; G	12	<i>Taraxacum officinale</i>	Poneasca; G	11
<i>Equisetum arvense</i>	Carașova; C	32	<i>Thymus pulegioides</i>	Steierdorf; C	240
<i>Galium verum</i>	Clocotici; C	287	<i>Thymus pulegioides</i>	Iabalcea; C	13
<i>Genista tinctoria</i>	Iabalcea; C	1	<i>Thymus pulegioides</i>	Poneasca mead.;G	2
<i>Hypericum perforatum</i>	Steierdorf; C	177	<i>Thymus pulegioides</i>	Secu lake; F	2
<i>Hypericum perforatum</i>	Poneasca mead.; G	4	<i>Thymus pulegioides</i>	Poiana Beții; C	1
<i>Hypericum perforatum</i>	Crainic; F	3	<i>Thymus pulegioides</i>	Șaua Crestății; C	24
<i>Hypericum perforatum</i>	Poneasca Mount.;G	18	<i>Thymus pulegioides</i>	Cioplăia Hill ; C	4
<i>Hypericum perforatum</i>	Gornice Hill; C	19	<i>Trifolium arvense</i>	Carașova; C	4
<i>Hypericum perforatum</i>	Cuceș; C	24	<i>Verbena officinalis</i>	Mărghitaș; C	26
<i>Hypericum perforatum</i>	to Doman; C	12	<i>Viola tricolor</i>	Bârzava mead.; F	9
<i>Leonurus cardiaca</i>	Mărghitaș; C	168	<i>Viola tricolor</i>	Carașova; C	4
<i>Leonurus cardiaca</i>	Caraș mead. ; C	2	<i>Viola tricolor</i>	Steierdorf; C	336
<b>Average Se content: 60 ± 87 <math>\mu\text{g}/\text{kg}</math></b>					

Note: C: limestone, F: phyllite, G: granite.

Vegetative organs of medicinal plants contain the highest Se amounts (in decreasing order: herbs, leaves, subterranean parts) while reproductive organs (flowers and fruits) contain less of the investigated element. In herbs, the Se content varies between 1  $\mu\text{g}/\text{kg}$  DM

(samples from several species) and 336  $\mu\text{g}/\text{kg}$  DM (wild pansy from Steierdorf region), its average being 60  $\mu\text{g}/\text{kg}$  DM. Selenium contents which greatly surpass the average were as well measured samples of agrimony, wild thyme, willow-herb and yellow bedstraw.

**Table 3.** The selenium content of leaves of medicinal plants ( $\mu\text{g}/\text{kg}$  dry plant).

Species	Collection site; geologic substrate	Se ( $\mu\text{g}/\text{kg}$ )	Species	Collection site; geologic substrate	Se ( $\mu\text{g}/\text{kg}$ )
<i>Allium ursinum</i>	Piatra Albă; C	147	<i>Plantago lanceolata</i>	Lisovacea; C	21
<i>Allium ursinum</i>	Lisvar Hill; C	11	<i>Plantago lanceolata</i>	Steierdorf; C	49
<i>Allium ursinum</i>	Poneasca mead.; G	1	<i>Rubus idaeus</i>	Poneasca Mount.; G	189
<i>Allium ursinum</i>	Poiana Florii; C	24	<i>Rubus idaeus</i>	Crainic mead.; F	21
<i>Allium ursinum</i>	Steierdorf; C	60	<i>Tussilago farfara</i>	Poneasca Mount.; G	6
<i>Althaea officinalis</i>	Caraș mead. ;C	97	<i>Urtica dioica</i>	Păuleasca; C	151
<i>Betula pendula</i>	Sekul; C	381	<i>Urtica dioica</i>	Poneasca Mount.; G	7
<i>Betula pendula</i>	Steierdorf; C	113	<i>Urtica dioica</i>	Crainic mead.; F	14
<i>Betula pendula</i>	Văliug lake; F	19	<i>Urtica dioica</i>	Lisovacea mead.; C	11
<i>Betula pendula</i>	Visochii Hill; C	131	<i>Urtica dioica</i>	Caraș mead.; C	28
<i>Corylus avellana</i>	Nermet; C	9	<i>Vaccinium myrtillus</i>	Văliug; F	140
<i>Corylus avellana</i>	Crainic mead.; F	7	<i>Viscum album</i>	Steierdorf; C	2
<i>Fragaria vesca</i>	Iabalcea; C	97	<i>Crataegus monogyna</i>	Lisovacea; C	93
<i>Fragaria vesca</i>	Sekul; C	1	<i>Crataegus monogyna</i>	Poneasca mead.;G	5
<i>Fragaria vesca</i>	Steierdorf; C	12	<i>Crataegus monogyna</i>	Sekul; C	5
<i>Fraxinus excelsior</i>	Padina Seacă; C	104	<i>Crataegus monogyna</i>	Iabalcea; C	7
<i>Fraxinus excelsior</i>	Ogașul Ursului; C	44	<i>Crataegus monogyna</i>	Steierdorf; C	22
<i>Plantago lanceolata</i>	Iabalcea; C	56	<i>Malva sylvestris</i>	Carașova ; C	4
<b>Average Se content: 58 ± 77 <math>\mu\text{g}/\text{kg}</math></b>					

Notes. In case of *Crataegus monogyna* and *Malva sylvestris*, the samples include both flowers and leaves (as they are used in phytotherapy).

C: limestone, F: phyllite, G: granite.

Relatively high Se amounts are also present in leaves, which contain on an average 58  $\mu\text{g}/\text{kg}$  DM (Table 3). Their Se concentration varies between 1-381  $\mu\text{g}/\text{kg}$  DM. Smallest Se contents are present in wood garlic leaves (site: Poneasca meadow) and wild

strawberry leaves (site: Sekul region), while birch leaves (site: Sekul region) contain the highest Se concentrations. Elevated Se contents were as well determined for two further samples of birch leaves and for raspberry leaves.

**Table 4.** The selenium content of subterranean parts of medicinal plants ( $\mu\text{g/kg}$  dry plant).

Species	Collection site; geologic substrate	Se ( $\mu\text{g/kg}$ )	Species	Collection site; geologic substrate	Se ( $\mu\text{g/kg}$ )
<i>Angelica archangelica</i>	Văliug; F	86	<i>Primula officinalis</i>	Lisvar Hill; C	94
<i>Cichorium intybus</i>	Lisovacea; C	11	<i>Saponaria officinalis</i>	Steierdorf; C	22
<i>Geum urbanum</i>	Răcăjdianu; C	125	<i>Symphytum officinale</i>	Clocitoare; C	1
<i>Geum urbanum</i>	Poneasca mead.; G	9	<i>Valeriana officinalis</i>	Miniș springs ; C	101
<i>Geum urbanum</i>	Lișcovu; F	1	<i>Valeriana officinalis</i>	Crainic; F	10
<i>Ononis spinosa</i>	Carașova; C	10	<i>Valeriana officinalis</i>	Păuleasca; C	28
<i>Primula officinalis</i>	Steierdorf; C	207		-	
<b>Average Se content: 54 + 63 <math>\mu\text{g/kg}</math></b>					

Note: C: limestone, F: phyllite, G: granite.

Roots and rhizomes contain, with an average of 35  $\mu\text{g Se/kg DM}$  (Table 4), a lower Se content than the aforementioned plant organs. Both highest and lowest

values were measured for wood avens roots originating from different sites (Lișcovu and Răcăjdianu).

**Table 5.** The selenium content of flowers and inflorescences of medicinal plants ( $\mu\text{g/kg}$  dry plant).

Species	Collection site; geologic substrate	Se ( $\mu\text{g/kg}$ )	Species	Collection site; geologic substrate	Se ( $\mu\text{g/kg}$ )
<i>Achillea millefolium</i>	Caraș mead.; C	108	<i>Sambucus nigra</i>	Poneasca Mount.; G	3
<i>Achillea millefolium</i>	Poneasca mead.; G	1	<i>Sambucus nigra</i>	Răcăjdianu; C	21
<i>Achillea millefolium</i>	Bârza mead.; F	1	<i>Tilia cordata</i>	Poneasca Mount. G	5
<i>Achillea millefolium</i>	Lisovacea; C	9	<i>Tilia cordata</i>	Lisvar; C	1
<i>Achillea millefolium</i>	Steierdorf; C	26	<i>Tilia tomentosa</i>	Baciului Valley; C	134
<i>Achillea millefolium</i>	to Doman; C	1	<i>Tilia tomentosa</i>	Secu lake; F	2
<i>Filipendula ulmaria</i>	Bârza mead.; F	101	<i>Verbascum phlomoides</i>	Mărghitaș; C	7
<i>Sambucus nigra</i>	Cârneala; C	112		-	
<b>Average Se content: 35 + 50 <math>\mu\text{g/kg}</math></b>					

Note: C: limestone, F: phyllite, G: granite.

Inflorescences and flowers display an average content of 35  $\mu\text{g Se/kg DM}$  (Table 5). Silver linden flowers with bracts from the Baciului Valley containing the highest Se amounts; several samples

contain very small quantities (1  $\mu\text{g Se/kg DM}$ ). Fruits are Se-poor and their average content is as low as 12  $\mu\text{g Se/kg DM}$  (Table 6).

**Table 6.** The selenium content of fruits of medicinal plants ( $\mu\text{g/kg}$  dry plant).

Species	Collection site; geologic substrate	Se $\mu\text{g/kg}$
<i>Cerasus avium (stipites)</i>	Nermet ; C	20
<i>Crataegus monogyna (fructus)</i>	Steierdorf ; C	10
<i>Juniperus communis (baccae)</i>	Poiana Mărghitașu Mare ; C	5
<b>Average Se content: 12 + 8 <math>\mu\text{g/kg}</math></b>		

Note: C: limestone, F: phyllite, G: granite.

## DISCUSSIONS

The essentiality of Se to plants is a controversial issue. Although Se has been shown to be an essential micronutrient for animals, bacteria, and probably algae, the question of whether Se is required for the growth of higher plants is still unresolved [27]. In order to investigate the essentiality of Se, two pathways have been pursued. First experiments investigated the presence of essential selenoproteins through radioactive labeling [1], but were unable to identify these proteins in higher plants. A second approach was to test for the presence of glutathione peroxidases (GPX), a major family of selenoproteins in animals. Evidence suggests that although GPX-like enzymes exist in higher plants, they are not selenoproteins. In contrast to animal GPX genes that contain a selenocysteine codon (UGA), the plant genes contain the cysteine codon (UGU) [11]. Plant GPX probably have different functions than their homologues in animals, as their activity is lower than 1% of animal GPX.

Selenium is taken up by plants mainly as selenate through a process of active transport via a sulfate transporter in the root plasma membrane. After absorption, selenate is converted into organic compounds such as selenomethionine, which is incorporated into the cellular proteins [28]. Plants can also take up organic Se forms. Excess Se is toxic to plants and causes stunting of growth, chlorosis, and premature death of the plant. Some Se-accumulating plants methylate Se as part of a detoxification mechanism. There is evidence that dimethyl selenide may be subject to foliar uptake, another route by which plants assimilate Se [27]. An interesting feature of particular higher plants is Se phytovolatilization, the ability to metabolize Se into volatile forms [15].

The Se content of plants differs widely among species. Most plants, grains and grasses rarely contain more than 30  $\text{mg Se/kg}$ , the general range being 0.05-1  $\text{mg/kg}$ . Cereals, vegetables and fruits from the European continent contain between 0.002-0.88  $\text{mg Se/kg}$  [23]. Occasionally, unusual high concentrations

of Se are reported in some species, known as Se accumulators. Such plants pertain to the genera *Astragalus*, *Stanleya*, *Morinda*, *Neptunia*, *Oonopsis* and *Xylorhiza*. They can accumulate from hundreds to thousands mg Se/kg dry mass in their tissues [27]. More recently, *Brassica* species (*B. juncea* and *B. napus*) were identified as Se-accumulator plants, reaching Se contents of several hundred mg Se/kg in their shoots when grown on soils with moderate levels of Se [6]. These species represent interesting candidates for the phytoremediation of Se-contaminated soils.

The Se content of the analyzed medicinal plants varies in large limits, from less than 1 µg/kg DM to 381 µg/kg, with a mean value of 43 µg/kg DM. Comparing these values with the above-mentioned concentrations from the literature, it can be stated that the medicinal plants from the investigated area contain low amounts of Se. The main reason for this situation is most probably represented by the low Se-content of soils from this region, especially as most of the samples were collected from limestone weathering soils with alkaline pH and good Se phytoavailability. A comparison of plants grown on Se-rich soils and Se-deficient soils [3, 9] pointed out significant differences (data in µg Se/kg DM): wheat – 130 versus 13, rye – 110 vs. 24; corn – 100 vs. 25; red clover – 80 vs. 15; potatoes – 55 vs. 12. In reference to these values it can be observed that the Se contents measured in the present study (68% of the samples contain beneath 50 µg Se/kg DM) are situated in the range of plants grown on Se-poor soils.

The collection of medicinal plants from sites with soils of different geological allowed us to point out the influence of the weathered rock on the Se content of plants. Systematic researches on this topic have been performed with the aid of indicator plants (rye, wheat, red clover) [3]. It was shown that the Se-richest flora

grows on loess soils, while plants growing on limestone weathered soils contain 50% less Se; species developing on phyllite and granite only contain 37% in comparison with plants from loess soils. In the present study it can frequently be observed that plants grown on limestone contain more Se than those vegetating on phyllite or granite. Such examples are (contents given in µg Se/kg DM): *Geum urbanum* rhizomes (lime: 125 µg Se/kg GU, granite: 9, phyllite 1); *Valeriana officinalis* rhizomes and roots (lime: 101 and 28, phyllite 10); *Epilobium parviflorum* herb (lime: 237 and 24, phyllite 13); *Equisetum arvense* herb (lime 129 and 32, phyllite 30, granite 12); *Hypericum perforatum* herb (lime: 177, 24 and 19, granite 18 and 4, phyllite 3). The same type of observation can be performed for *Origanum vulgare*, *Taraxacum officinale*, *Thymus pulegioides*, *Allium ursinum*, *Betula pendula*, *Urtica dioica*, *Achillea millefolium*, *Sambucus nigra*. Comparing the average Se content of plants grown on limestone with the Se content of plants vegetating on other substrates, a highly significant difference results ( $p < 0.001$ ).

In the investigated plants, Se mainly accumulates in vegetative organs (roots, stems, leaves); the difference between the Se content of these plant parts and of reproductive organs (flowers, fruits) is significant ( $p > 0.05$ ). Among the plants able to accumulate higher Se amounts, when this element is present in adequate amounts in the soil we can cite: *Betula pendula* (the only species where 3 samples collected from limestone weathered soils contain more than 100 µg Se/kg), *Primula officinalis*, *Agrimonia eupatoria*, *Viola tricolor*, *Galium verum*, *Epilobium parviflorum*, *Lythrum salicaria*. The relatively high Se contents as well as consistent amounts of flavonoids from birch, agrimony and yellow bedstraw underline the value of these plants in the auxiliary treatment of various free-radical mediated diseases.

Table 7. The selenium content of some aqueous extracts obtained from medicinal plants

Species – plant part	Se (µg/kg)		extraction yield (%)
	in plant product	extracted through decoction*	
<i>Cichorium intybus</i> (chicory) - roots	11	9.1	83
<i>Equisetum arvense</i> (horsetail) - herb	129	90	70
<i>Hypericum perforatum</i> (St John's wort) – herb**	4	2	50
<i>Ononis spinosa</i> (restharrow) - roots	10	4	40
<i>Viola tricolor</i> (wild pansy) - herb	336	92	27
<i>Filipendula ulmaria</i> (meadowsweet) - flowers	101	21	21
<i>Crataegus monogyna</i> (hawthorn) – leaves and flowers	5	1	20
<i>Cichorium intybus</i> (chicory) - herb	64	10	16
<i>Primula officinalis</i> (cowslip) - rhizomes	94	13	14
<i>Sambucus nigra</i> (elder) - flowers	112	15	13
<i>Althaea officinalis</i> (marshmallow) - leaves	97	9.1	9
<i>Achillea millefolium</i> (yarrow) - flowers	108	10	9
<i>Leonurus cardiaca</i> (motherwort) - herb	168	15	9
<i>Taraxacum officinale</i> (dandelion) - herb	188	15	8
<i>Thymus pulegioides</i> (wild thyme) - herb	240	15	6
<i>Epilobium parviflorum</i> (willow herb) - herb	237	11	5
<i>Valeriana officinalis</i> (valerian) – rhizomes and roots	28	1	4

Note: \* Values represent the extractable V amount through decoction (15 minutes) from the indicated vegetal product; preparations were made of 4% plant material in bidistilled water. \*\* Herbs (*herba*) represent the flowering aerial parts of medicinal plants.

Aqueous extracts of medicinal plants enjoy a high acceptance and popularity in the phytotherapy of our

country. For this reason, we evaluated the proportion in which medicinal plants transmit their Se charge to

herbal teas. Results indicate a large variation of the extraction yield, according to the species subjected to decoction (Table 7). The easiest passage into water (>70%) is specific to Se from chicory roots and horsetail herb, while Se from willow herb and valerian roots can be extracted in the lowest proportion. These variations can be explained by each plant's different chemical composition, where saponins, tannins, mucilages, flavonoids etc. create specific pH values and redox potentials, or involve Se in complex combinations with low solubility. A correlation between the facility of the extraction and the type of the plant organ or the presence of a certain type of active principle could not be achieved in the present study.

Future studies are necessary for the analysis of the Se-status of the Romanian flora. The present study indicates that in the researched area both flora and soils are Se-poor. As Se is an ultratrace element of fundamental importance for human physiology, this situation might have implications for the health status of the population from this region.

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