Situated between mercury and lead in the sixth period of the Periodic Table, thallium (Tl) is a heavy element with a scarce occurrence in the upper earth crust (0.1-0.5 μg kg⁻¹). Its ionic radius is identical to that of Rb⁺ and close to that of K⁺. For this reason, Tl is often associated with Rb and K in the environment, and has a resembling geochemical behaviour [1].

Thallium is more toxic to humans than mercury, cadmium and lead [2]. It substitutes K⁺ in enzymes, and interferes with its transport across membranes, altering the transmission of nerve impulses and muscle excitability [3]. Tl binds to membrane phospholipids and disrupts lipid packing; it depletes riboflavin and causes thiamin deficiency resulting in neuropathies. Its capacity to interact with thiol groups leads to the inhibition of a variety of enzymes and triggers oxidative stress via binding to glutathione, a non-protein thiol involved in the detoxification processes and defense against reactive oxygen species. The most common effects of a chronic Tl intoxication are polyneuropathy and psychiatric alterations [4]. Mutagenicity, carcinogenicity and teratogenicity of the element have also been described [5]. For these considerations, threshold contents for Tl in occupational environments and drinking water are subject to regulations by the World Health Organization and the US Environmental Protection Agency [6,7]. In case of foodstuffs no threshold values have been set yet by the WHO or governmental agencies. Proposed upper contents of Tl in vegetables and fruits are 100 μg kg⁻¹ dry weight, being followed by aerial parts, flowers and leaves with 19.3, 17.2 and 16.6 μg Tl kg⁻¹, respectively. The highest Tl content was measured for the Boraginaceous species Echium vulgare, which may be used as a biomonitor of anthropogenic Tl contamination. This study shows that the Tl content of the investigated plants does not pose health risks, provides useful reference data for wild-growing plants from unpolluted sites, and documents the naturally low environmental level of Tl in South Western Romania.

**Keywords:** thallium, medicinal plants, ICP-MS, biomonitor

The research of thallium in the food chain is of high significance to human health. Roots contain the highest Tl content, followed by aerial parts, flowers and leaves with concentrations of 19.3, 17.2 and 16.6 μg Tl kg⁻¹, respectively. Tl is liberated from the plant products during decoction, as herbal teas are a major form of administration in phytotherapy. The significance of the Tl amounts present in herbs and teas to human health is discussed.

**Experimental part**

**Plant material**

Hundred twenty-five samples representing plant organs of 56 medicinal species employed in phytotherapy were collected from the wild flora of the Aninei Mountains (South-West of Romania). The plants were gathered at altitudes of 400-900 m, from unpolluted sites. Name of the sites are given according to the maps of Sencu (1978) [12]. After collection, the samples were dried at ambient temperature and deposited in cotton sacks. Previous to the determination of Tl content, plants were brought to powder and concentrations are routinely checked, in the case of Tl there are no regulations in prime matters intended for phytomedicines, and its monitoring is not performed. The present research provides for the first time data on the Tl content of over 50 species of wild-growing medicinal plants, measured through ICP-MS, and evaluates the results in the context of their significance to human health. Roots contain the highest Tl contents with an average of 25.5 μg kg⁻¹ dry weight, being followed by aerial parts, flowers and leaves with 19.3, 17.2 and 16.6 μg Tl kg⁻¹, respectively. The highest Tl content was measured for the Boraginaceous species Echium vulgare, which may be used as a biomonitor of anthropogenic Tl contamination. This study shows that the Tl content of the investigated plants does not pose health risks, provides useful reference data for wild-growing plants from unpolluted sites, and documents the naturally low environmental level of Tl in South Western Romania.

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**Flora and Significance to Human Health**

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important amounts of minerals. Levels of toxic elements
encapsulated herbal powders and extracts contain
stems from organic constituents, the content in various
of many chronic diseases. While the therapeutic effect
multipotent effects, suitable for the long-lasting treatment
growing interest due to a generally higher safety and
matter for phytotherapeutic preparations, receiving a

Results and discussions

In order to evaluate the proportion in which Tl passes
into solution, we prepared decoctions out of 16 plant
products, obtained as follows: 50 mL bidistilled water were
added to 2.000 g dried herb, and heated to boiling; 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 Tl passes
into solution, we prepared decoctions out of 16 plant
products, obtained as follows: 50 mL bidistilled water were
added to 2.000 g dried herb, and heated to boiling; the
temperature of 100°C was maintained for 15 min. 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.

Method of analysis

As a first step, a semi-quantitative analysis was performed, allowing the estimation of the Tl concentration
ranges in the digestion solutions of the plant materials. Quantitative determinations were carried out with the aid
of a calibration curve using ICP Multi Element Standard
Solution XXI CertiPUR Merck, diluted to obtain optimal
measurement range (between 0.05 - 10.00 μg L⁻¹). Internal
standard was rhodium. The limit of detection for Tl was
0.05 μg L⁻¹. Accuracy of data has been verified by parallel
analysis of a certified reference material.

Results and discussions

Medicinal and aromatic plants are an important prime
matter for phytotherapeutic preparations, receiving a
growing interest due to a generally higher safety and
multipotent effects, suitable for the long-lasting treatment
of many chronic diseases. While the therapeutic effect
stems from organic constituents, the content in various
mineral elements should not be overlooked. Herbal teas,
capsulated herbal powders and extracts contain
important amounts of minerals. Levels of toxic elements
like Pb, Cd, Hg and As in plant prime matters intended for
medicinal use are subject to regulations and routinely
checked [13,14]. Although Tl is highly toxic, its level in
medicinal plants is up to the present not subject to
limitations and, furthermore, reference data are missing
for this category of plants.

In the present study, the analyzed plant organs contain
Tl amounts ranging from 0.01 (underground parts of Gei
derhizoma) to 278.1 μg kg⁻¹ dry weight (aerial parts of Echium
vulgare), with an average of 17.5 μg kg⁻¹ GU. The vast
majority of the samples (92.8%) contain less than 50 μg Tl
kg⁻¹: 28.8% contain 10-50 μg Tl kg⁻¹, 33.6% have a Tl level
of 5-10 μg kg⁻¹, the remainder of 30.4% only contain 0.01-5
μg Tl kg⁻¹. The subterranean parts have the highest Tl
levels, with an average of 25.5 μg kg⁻¹ (table 1), being
followed by aerial parts, flowers and leaves with 19.3, 17.2
and 16.6 μg Tl kg⁻¹, respectively (tables 2-4). The fruits
and seeds contain the lowest Tl amounts (table 5).

Recent literature data on the Tl content of plants from
unpolluted areas are not available. Based on earlier works
of Geilmann et al. (1960) and Dvornikov et al. (1973, 1976),
the WHO summarizes that usual Tl concentrations in
plants are much less than 0.1 mg kg⁻¹ DW or 1 mg kg⁻¹ ash
following concentration ranges in plants grown on
unpolluted sites (given in μg/kg DW); vegetables and fruits:
20-125, clover: 8-10, hay 20-25 μg kg⁻¹ GU. In areas with
naturally high Tl levels, contents of several gram/ash
are common [6]. Compared to the above, Tl concentrations
measured in the medicinal plants during the current survey
may be considered low, typically for unpolluted areas with a
normally low geogenetic Tl occurrence. In several samples,
Tl content marks important variations of up to two orders
of magnitude, according to the site of collection. A
correlation between the type of the geologic substrate and
the Tl content of plants could not be observed although it is
known that Tl levels are higher in acidic, granite rocks (0.6-
2.3 ppm) than in lime (0.01-0.14 ppm) [8]. The lack of
such a correlation in the current study is most probably
due to important local differences of Tl occurrence,
individually of the weathering rock. Medicinal plants
containing far above the average Tl content are Echium
vulgare (aerial parts), Rubus idaeus (leaves), Chelidonium
majus (aerial parts), Achillea millefolium (flowers), Thymus
pulegioides (herb), and Primula veris (roots). The literature
does not mention any of these species as Tl accumulators.
They could potentially be employed as biomonitors of
anthropogenic Tl contamination. Up to the present, it is
Brassicaceae species (Biscutella laevigata, Iberis
intermedia) which have received the widest attention with
regard to their Tl content; they have a remarkable capacity

<table>
<thead>
<tr>
<th>Species</th>
<th>Collection site; Geologic substrate</th>
<th>Tl (μg kg⁻¹)</th>
<th>Species</th>
<th>Collection site; Geologic substrate</th>
<th>Tl (μg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angelica archangelica</td>
<td>Vălug area; Ph</td>
<td>4.7</td>
<td>Primula officinalis</td>
<td>Lisvar Hill; L</td>
<td>77.9</td>
</tr>
<tr>
<td>Cichorium intybus</td>
<td>Lisovacea; L</td>
<td>21.0</td>
<td>Saponaria officinalis</td>
<td>Steierdorf area; L</td>
<td>30.4</td>
</tr>
<tr>
<td>Geum urbanum</td>
<td>Răchdiun; L</td>
<td>16.3</td>
<td>Symphytum officinalis</td>
<td>at Cloicoare; L</td>
<td>12.3</td>
</tr>
<tr>
<td>Geum urbanum</td>
<td>Poneasca mead; G</td>
<td>41.1</td>
<td>Valeriana officinalis</td>
<td>Minș spring; L</td>
<td>8.2</td>
</tr>
<tr>
<td>Geum urbanum</td>
<td>Lioceu; Ph</td>
<td>0.01</td>
<td>Valeriana officinalis</td>
<td>Crainic; Ph</td>
<td>54.2</td>
</tr>
<tr>
<td>Ononis spinosa</td>
<td>Carășova area; Ph</td>
<td>22.5</td>
<td>Valeriana officinalis</td>
<td>Puleasa; L</td>
<td>34.4</td>
</tr>
<tr>
<td>Primula officinalis</td>
<td>Steierdorf area; L</td>
<td>8.6</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average Tl content: 25.5 ± 22.1

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

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to store and tolerate Tl due to the affinity of this element for thiolic glucosinolates [16,17].

In humans, the usual Tl intake in non polluted areas is 2-5 μg per day [18]. Provisions for the Tl content of drinking water have been issued by the US Environmental Protection Agency, stating that the maximum level at which no known adverse effects on human health are anticipated, is 2 μg L⁻¹ [7]. The Office of Environmental Health Hazard Assessment estimated a content of 0.1 μg Tl L⁻¹ that would pose no significant health risk to individuals consuming water on a daily basis over a lifetime [3]. With regard to these numbers, we performed an evaluation of the Tl content in some teas, prepared through decoction of medicinal plants selected from the ones analyzed with regard to their Tl levels. Extraction yields proved to be highly variable between species, ranging from 5.3% (horsetail herb) to 88.7% (valerian roots). Based on the Tl amounts extracted through decoction (table 6) it can be concluded that herbal teas prepared from 6g plant (the equivalent of 3 cups per day prepared from 2 g each) may supply up to 0.234 μg Tl per day under a highly bioavailable form. The Tl concentration of aqueous extracts prepared from the selected medicinal plants is situated in the range from 0.04 to 1.56 μg L⁻¹, below the maximum level at which no known adverse effects on human health are anticipated for drinking water.
Conclusions

The analysis of 125 samples of various medicinal plants collected from the wild flora of South-Western Romania with regard to their Tl content shows that the levels of this heavy element may be considered low, typical for unpolluted areas with a normally low geogenous Tl occurrence. Several medicinal plants accumulating Tl could be highlighted: *Echium vulgare, Rubus idaeus, Chelidonium majus, Achillea millefolium, Thymus pulegioides,* and *Primula veris*. They could potentially be employed as biomonitors of anthropogenic Tl contamination. Yields of Tl extraction from the plant matrix...
onto herbal teas proved to be highly variable between species, ranging from 5.3 to 88.7%, but stable for the same species. The Tl concentration of aqueous extracts prepared from the selected medicinal plants was below the maximum level at which no known adverse effects on human health are anticipated for drinking water.

Acknowledgement. The authors wish to thank Agrar- and Umweltanalytik Jena for assistance in ICP-MS measurements.

References


Manuscript received: 24.04.2014