RESEARCH UPON THE HEAVY METALS CONTENT OF SOME *SENECIO* SPECIES

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ABSTRACT. The analysis of heavy metals in the roots, aerial parts and flowers of three Senecio species (S. jacobaea, S. vernalis, and S. vulgaris) has been performed. The mean levels of heavy metals in vegetal dried samples were in normal limits. The results indicate that there is not any real danger by utilization of galenic forms of Senecionis herba. Differences between the species depend on the presence of organic compounds with ligand character and on the environmental conditions.

Keywords: *Senecio* sp., heavy metals, content

INTRODUCTION

Senecio jacobaea L. (common ragwort, tansy ragwort), *S. vernalis* Waldst. et Kit. (Eastern groundsel, spring groundsel) and *S. vulgaris* L. (common groundsel, old-man-in-the-spring) species, of *Asteraceae* family, are native in: Eurasia, North America, Australia, New Zealand, Argentina, and Northern Africa. They are herbaceous, common in Romania's flora, along roadsides, waste grounds, forests and crops. They grow in all cool and high rainfall areas, from the plain to the mountains zone. *S. jacobaea* is perennial. *S. vernalis* and *S. vulgaris* are annual or biennial (Ciocârlan, 2000).

Senecio species contain some active principles as follows: pyrrolizidine alkaloids, flavonosides, volatile oils, sterols, triterpenes, carotenoids, heteroglycans, catechic tannin, lipids (in the seeds), organic acids, sugars, vitamins, mineral salts (Bruneton, 1995; Ciulei *et al.*, 1993; Hegnauer, 1999; Mogoşanu *et al.*, 2003; Mogoşanu, 2005; Röder, 1995).

Pyrrolizidine alkaloids have been reported by the WHO to be toxic to animals and humans. Honey collected over *Senecio* sp. has been found to contain small quantities of pyrrolizidine alkaloids. However, the flowering aerial parts are used in phytotherapy under the generic name of *Senecionis herba* (Bruneton, 1995; Ciulei *et al.*, 1993; Hegnauer, 1999; Mogoşanu *et al.*, 2003; Mogoşanu, 2005; Röder, 1995).

The danger of *Senecio* sp. is that the alkaloids could have a cumulative effect. The result, if sufficient quantity is consumed, can be irreversible liver cirrhosis. Signs that a horse has been poisoned include yellow mucus membranes, depression, and lack of coordination. Sheep and goats suffer the same process of liver destruction, but at a reduced rate to horses and pigs. There is no known antidote or cure to poisoning, but at examples are known from the scientific literature of horses making a full recovery once consumption has been stopped. *Senecio* sp. posses little risk to the livers of humans. Some sensitive individuals can suffer from an allergic reaction because of the sesquiterpene lactones content, which can cause dermatitis (Bruneton, 1995; Ciulei *et al.*, 1993; Delaveau, 1985; Mogoşanu, 2005; Zanoschi *et al.*, 1981).

The plants are astringent, diaphoretic, diuretic, emmenagogue, galactagogue, antidiarrhoeal and expectorant. An emollient poultice is made from the leaves. The juice of the plants is cooling and astringent. It is used as a wash in burns, sores, cancerous ulcers and eye inflammations. It makes a good gargle for ulcerated mouths and throats and is also said to take away the pain of a bee sting. A decoction of the root is said to be good for treating internal bruises and wounds. A homeopathic remedy is made from the plants. It is used in the treatment of dysmenorrhoea and other female complaints, internal haemorrhages and other internal disorders (Borza, 1968; Bruneton, 1995; Butură, 1979; Ciulei *et al.*, 1993; Mogoşanu, 2005).

The control of the heavy metals contents in medicinal and aromatic plants represents one of the

factors for the evaluation of their quality. Since these plants originate from different growing areas, great differences in the uptake and concentrations of heavy metals in the plant tissue can be expected. The high heavy metal content in some medicinal plants arises from their ability to accumulate particular metals, especially cadmium. However, high heavy metals uptake can also be found in growing areas located in mountain regions, due to certain properties of these soils, such as acidity and/or the presence of metal-bearing minerals, which favour the mobility of heavy metals in a soil and their high availability to plants (Kalra, 1998).

In the specialty papers we found a single citation regarding the mineral content of *S. jacobaea*: 23.24% ash, which contains 40% K_2O, 14% Cl, 14.6% CaO, 10.7% SO_4^{2-}, 8.3% P_2O_5, 6.4% Na_2O, 4.6% MgO, 3% Fe_2O_3, 1.7% SiO_2 (Wehmer, 1931).

MATERIALS AND METHODS

Sampling

The number of plants to sample in a particular situation depends on the general condition of the plants, soil homogeneity, and the purpose for which the analysis results will be used. To ensure representation, sampling as many as practical is recommended, collecting samples during a particular time of day and under calm climatic conditions (Kalra, 1998).

From each of three *Senecio* species twenty vegetal samples were collected at the flowering, as follows: *S. jacobaea*, in August 2001, from the surroundings of Scaesti Village (Dolj); *S. vernalis*, in April 2002, from Craiova (Romanescu Park); *S. vulgaris*, in June 2002, from the Botanical Garden of the University of Craiova.

Preparation of plant tissue for analysis

Sample preparation is critical in obtaining accurate data and reliable interpretation of plant analysis results. The vegetal products should be processed during decontamination, drying, particle-size reduction, storage and organic matter destruction. Plant material must be cleaned and free of extraneous substances, including soil and dust particles that may influence analytical results (Kalra, 1998).

The decontamination process must be thorough while still preserving sample integrity. Decontamination procedures involving washing and rinsing with deionized water and 0.2% detergent solution (non-phosphate), should only be used for fresh, fully turgid plant samples.

After decontamination, water is removed from plant tissue, at temperatures under 60^0C, to stop the enzymatic reactions and to stabilize the samples. Plant tissue samples are reduced to 0.5 to 1.0 mm particle size to ensure homogeneity and to facilitate organic matter destruction (Kalra, 1998).

Gravimetric determination of ash

The ash represents the residue obtained through the dry ashing of a matter, being made by inorganic compounds. Dry-ashing is conducted in a muffle furnace at temperature 500 to 550^0C for four to eight hours. For tissues high in carbohydrates and oils, ashing aids may be required to achieve complete decomposition of organic matter.

At the end of the ashing period, the vessel is removed from the muffle furnace, cooled, and the ash is dissolved in nitric acid. The final solution is diluted as needed to meet the range requirements of the analytical procedure or instrument utilized (Kalra, 1998).

Weigh 0.5 to 1.0 g dried plant material that has been ground and homogenized into a high-form, 30 mL porcelain crucible. Samples were placed in a cool muffle furnace.

Temperature control of the furnace was set to allow gradual increase (2 hours) in the ashing temperature and maintain for 4 to 8 hours. After that, the furnace was turned off to allow samples to cool (1 hour). Then, the ash is weighing on analytical balance nearest 0.1 mg.

High temperature oxidation. Heavy metals detection

This method prepares plant tissue for the quantitative determination of the content of Cu^{2+}, Zn^{2+}, $Fe^{2+/3+}$, Mn^{2+}, Ni^{2+}, Pb^{2+}, Cr^{3+}, by atomic absorption spectrometry (AAS), utilizing high-temperature dry oxidation of the organic matter and dissolution of the ash with 4% nitric acid. The method detection limit is approximately 0.04%. The method is generally reproducible within ±7% (Kalra, 1998).

The tissue samples (*radix*, *herba*, *flos*) were prepared in the above mentioned manner. Heavy metals content was determined using analytical balance, porcelain crucibles, muffle furnace, volumetric labware, deionized water, standard calibration solutions, and an AAS Varian–6L type.

Five standard calibration dilutions (0.001 mg/L to 2 mg/L) were prepared starting from 5 mg/L reference solutions diluted with 4% nitric acid.

RESULTS AND DISCUSSION

The results of AAS analysis are given as mean and standard deviation (**Tables 1–3** and **Figure 1**).

The maximum limits of heavy metals allowed in plants for adequate growing and development are the followings: 3 mg% Cu^{2+}, 10 mg% Zn^{2+}, 5 mg% Mn^{2+}, 100 mg% $Fe^{2+/3+}$, 0.80 mg% Ni^{2+}, 50 mg% Pb^{2+} and Cr^{3+} (Kalra, 1998).

In the vegetal products obtained from above mentioned *Senecio* species the content of the heavy metals can be considered as normal.

All samples contain Pb^{2+} and Cr^{3+}, markers for soil and air pollution. The levels of Pb^{2+} (normal limits) in vegetal tissues samples appear because the plants collected were relatively closely to roads (cars circulation).

High levels of Pb^{2+} and Cr^{3+}, but in normal limits, have been determined in roots, because their intake from soil or aerial parts. This is an important finding, because only the aerial parts obtained from *Senecio* species are usually used as medicinal products.

The aerial parts contain high levels of Mn^{2+}, $Fe^{2+/3+}$ and Ni^{2+} then roots and flowers. In the flowers, Cu^{2+}

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and Zn^{2+} attain high concentrations, probably as consequence of the bioinorganic mechanisms during the flowering period and of the soil acidity. Generally, for most plants the concentrations of some heavy metals are higher in the roots then in the above-ground parts.

AAS analysis confirmed indirectly that the samples were collected from mature *Senecio* species, during the flowering period, when appear complex combinations with divalent (Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}) or trivalent (Fe^{3+}, Cr^{3+}) metallic cations.

The soil analysis and the avoiding of collecting samples from polluted zones are recommended for vegetal medicinal products with internal uses as powders and extracts. Therefore, the only safe way to prevent high intake of heavy metals through galenic forms of *Senecionis herba* is quality control of the raw materials before their further utilization. Special attention has to be paid if the medicinal product originates from mineral-carriers of heavy metals and low soil pH, which could induce high content of heavy metals in the raw material (aerial parts).

Table 1

HEAVY METALS CONTENT OF S. JACOBAEA SAMPLES

Heavy metals	*Senecionis jacobaeae radix*	*Senecionis jacobaeae herba*	*Senecionis jacobaeae flos*
	mg%	*mg%*	*mg%*
Cu^{2+}	3.324 ± 0.2	4.805 ± 0.3	6.956 ± 0.4
Zn^{2+}	2.135 ± 0.2	1.583 ± 0.1	4.241 ± 0.3
Mn^{2+}	1.879 ± 0.1	3.366 ± 0.2	1.230 ± 0.1
$Fe^{2+/3+}$	15.628 ± 1.5	35.721 ± 3.1	22.476 ± 2.1
Ni^{2+}	0.085 ± 0.002	0.158 ± 0.01	0.073 ± 0.002
Pb^{2+}	10.767 ± 0.6	5.368 ± 0.4	1.240 ± 0.1
Cr^{3+}	1.273 ± 0.1	0.936 ± 0.06	0.528 ± 0.04
dried sample [g]	0.6999 ± 0.0002	0.5117 ± 0.0001	0.7964 ± 0.0003
ash [g]	0.1250 ± 0.0002	0.0463 ± 0.0002	0.0675 ± 0.0002
% dry ashing residue	17.86 ± 1.2	9.05 ± 0.5	8.48 ± 0.5

Table 2

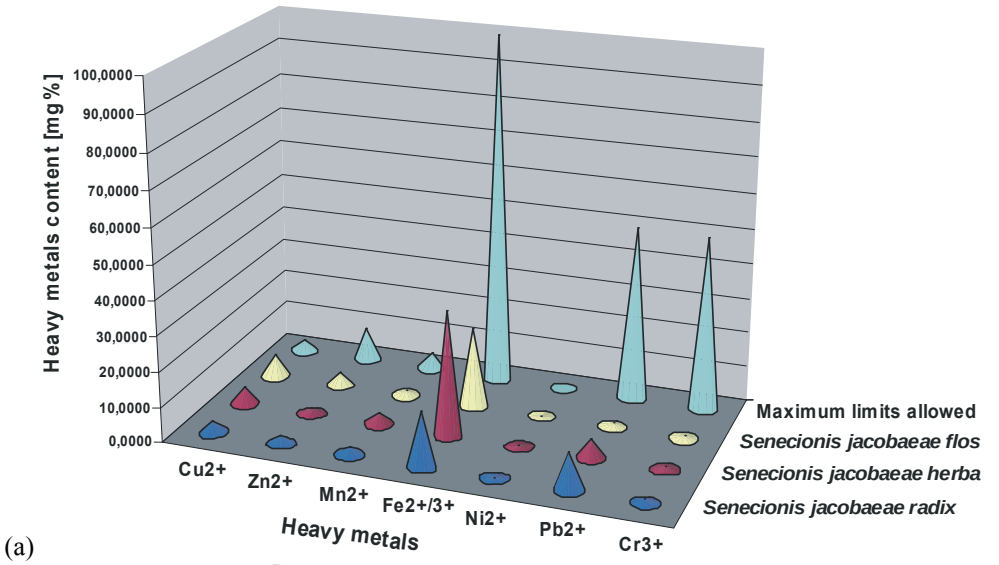
HEAVY METALS CONTENT OF S. VERNALIS SAMPLES

Heavy metals	*Senecionis vernalis radix*	*Senecionis vernalis herba*	*Senecionis vernalis flos*
	mg%	*mg%*	*mg%*
Cu^{2+}	3.015 ± 0.2	3.870 ± 0.2	4.512 ± 0.3
Zn^{2+}	2.210 ± 0.2	1.438 ± 0.1	3.615 ± 0.2
Mn^{2+}	1.765 ± 0.1	3.250 ± 0.2	1.100 ± 0.1
$Fe^{2+/3+}$	19.332 ± 1.6	40.728 ± 3.3	27.350 ± 2.5
Ni^{2+}	0.050 ± 0.002	0.247 ± 0.01	0.115 ± 0.01
Pb^{2+}	15.877 ± 1.5	8.418 ± 0.5	2.380 ± 0.2
Cr^{3+}	1.118 ± 0.1	0.825 ± 0.05	0.247 ± 0.02
dried sample [g]	1.0718 ± 0.0001	1.1547 ± 0.0002	0.3910 ± 0.0002
ash [g]	0.1971 ± 0.0003	0.1167 ± 0.0001	0.0396 ± 0.0002
% dry ashing residue	18.39 ± 1.2	10.11 ± 0.5	10.13 ± 0.5

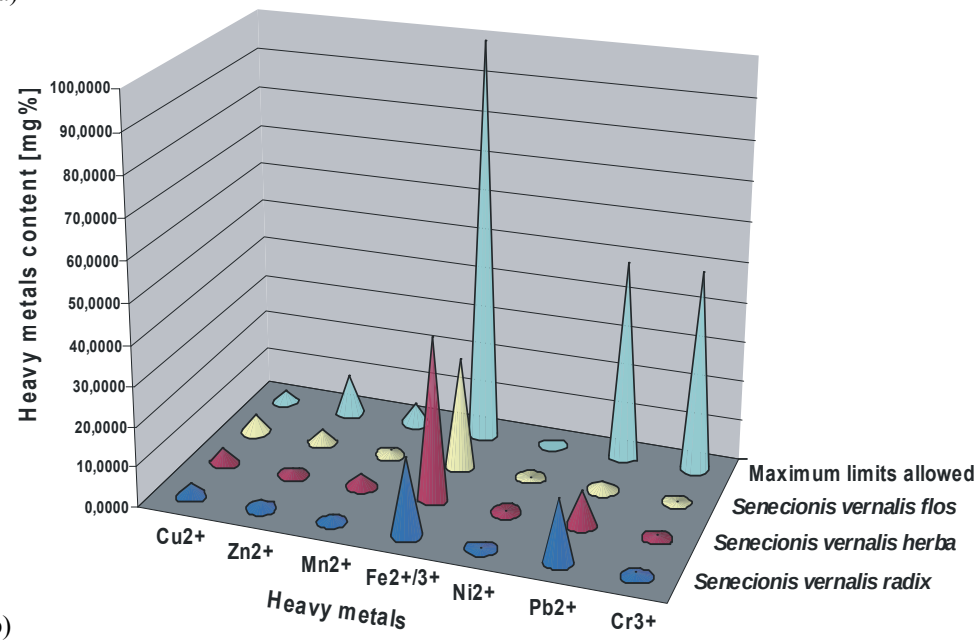
Table 3

HEAVY METALS CONTENT OF S. VULGARIS SAMPLES

Heavy metals	*Senecionis vulgaris radix*	*Senecionis vulgaris herba*	*Senecionis vulgaris flos*
	mg%	*mg%*	*mg%*
Cu^{2+}	2.142 ± 0.2	2.787 ± 0.2	3.231 ± 0.3
Zn^{2+}	2.037 ± 0.2	1.235 ± 0.1	3.419 ± 0.3
Mn^{2+}	1.920 ± 0.1	2.987 ± 0.2	1.037 ± 0.1
$Fe^{2+/3+}$	23.823 ± 1.7	70.935 ± 5.9	32.154 ± 3.0
Ni^{2+}	0.105 ± 0.01	0.208 ± 0.02	0.173 ± 0.01
Pb^{2+}	14.267 ± 1.5	6.369 ± 0.4	1.438 ± 0.1
Cr^{3+}	1.032 ± 0.1	0.756 ± 0.05	0.387 ± 0.02
dried sample [g]	0.4489 ± 0.0002	0.9315 ± 0.0002	0.8762 ± 0.0002
ash [g]	0.0653 ± 0.0001	0.1161 ± 0.0003	0.1036 ± 0.0003
% dry ashing residue	14.55 ± 0.9	12.47 ± 0.7	11.83 ± 0.6



(a)



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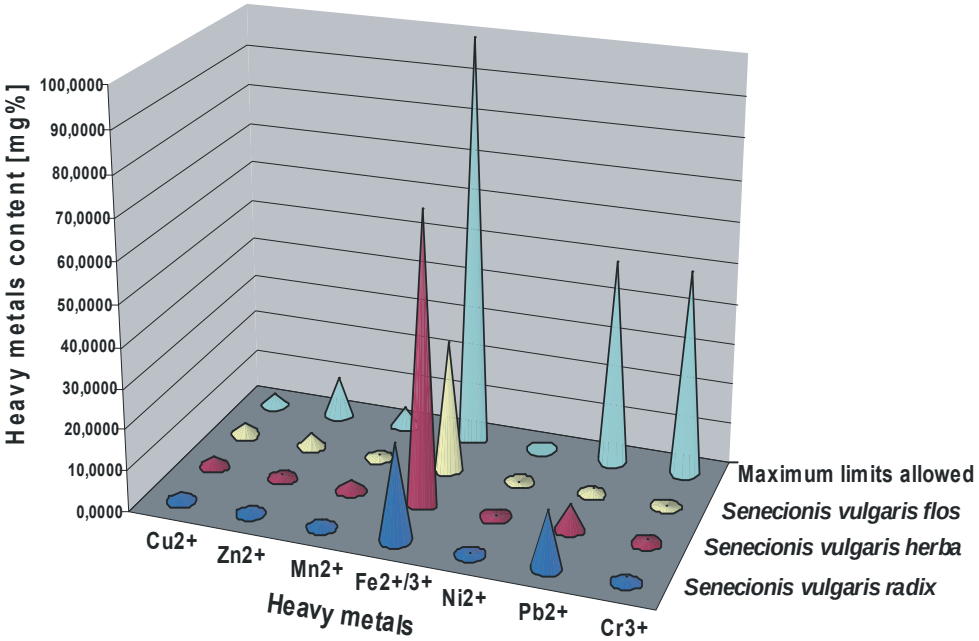

(c)

Fig. 1 Maximum limits allowed and heavy metals content of (a) *S. jacobaea*, (b) *S. vernalis* and (c) *S. vulgaris* samples

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It should be noted that for nearly every element above the optimum concentration, there is an adequate zone or sufficiency range, which indicates that most elements can be taken up at levels greater than needed for "optimum" yield before yields are decreased due to an excess or an imbalance with other elements occurs. Nutrient concentrations that produce the maximum or optimum yields have been established as the critical or optimum levels (Kalra, 1998).

The elemental content of a plant is not a fixed entity, but varies from month to month, day to day, and even from four to hour, as well as differing between various parts of the plant itself. A plant part at a specific location on the plant obtained at a definite stage of growth (based on physiological age) constitutes the sampling parameters. In general, tissues that are either physiologically young and undergoing rapid change in elemental content and those past full maturity should not be sampled. The plant part selected and the time of sampling must correspond to the best relationship that exist between its elemental content and yield or the physical appearance of the plant (Kalra, 1998).

Plant analysis can play a major role when diagnosing mineral nutrition problems, whether for research purposes or for solving practical field problems. Most of the essential elements required by crops and the climatic, genetic, cultural, and management factors that influence plant growth, development, and maturation must be factored into the interpretation of a plant analysis result. All these factors are interactive. While plant analysis is not the final answer with respect to regulating the mineral nutrition of plants, it has been and will continue to be one of the most useful tools leading to improved crop production and quality (Kalra, 1998).

CONCLUSIONS

The content of some heavy metals (Cu^{2+}, Zn^{2+}, Mn^{2+}, $Fe^{2+/3+}$, Ni^{2+}, Pb^{2+}, Cr^{3+}) of the vegetal products (*radix*, *herba*, *flos*) collected from three *Senecio* species (*S. jacobaea*, *S. vernalis* and *S. vulgaris*) has been established using atomic absorption spectrometry analysis.

The content of the heavy metals can be considered in normal limits, even for Pb^{2+} and Cr^{3+} markers for soil and air pollution.

High levels of Mn^{2+}, $Fe^{2+/3+}$ and Ni^{2+} have been determined in the aerial parts then in the roots and flowers. The flowers contain high levels of Cu^{2+} and Zn^{2+}.

The samples have been collected during the flowering period, when appearing complex combinations with divalent (Cu^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Pb^{2+}) or trivalent (Fe^{3+}, Cr^{3+}) metallic cations.

The results indicate that there is not any real danger by utilization of galenic forms of *Senecionis herba*.

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