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REGULAR ARTICLE

Heavy metals accumulation and translocation in native plants grown on tailing dumps and human health risk

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Abstract The heavy metal concentration in plant tissues of *Ranunculus ficaria, Plantago major, Taraxacum officinale*, and *Achillea millefolium,* frequently consumed or used in traditional medicine, collected from one of radioactive area of Romania, not been previously reported by any research group. The content of Cr, Mn, Ni, Cu, Zn, Cd, Pb were determined by ICP-MS. To evaluate the level of pollution, the plants are examined to determine the EDI, HRI and TTHQ values, to reach a judgment about whether their consumption is risky or not in terms of human health. The high amounts of Cd, Mn and Pb, in tissues of *Taraxacum officinale* and *Plantago major*, lead to the fact that the ecosystem in which these species are growing should be evaluated by the authorities in terms of environmental pollution. DIM and HRI data showed that *A. millefiori* and *R. ficaria* can be safely used by locals, while *T. officinale* and *P. major* are thought to pose a risk in terms of heavy metals. Accumulation of metals by both roots and leaves in *T. officinale* and *P. major* was proportional to the metal concentration in the tailings dumps, while Cr, Mn, Cd, and Pb content exceeded the maximum permissible daily levels.

Keywords Heavy metal · Native plant · Transfer factor · Translocation factor · Daily intake metals · Health risk index

Abbreviations

BaF	Bioaccumulation Factor / Transfer Factor
CR	Carcinogenic Risk
CSF	Cancer Slope Factor
DIM	Daily Intake Metal
EDI	Estimated daily intakes
HRI	Human Risk Index
ICP-MS	Inductive Coupled Plasma Mass Spectrometry
LOD	Limit of Detection
LOQ	Limit of Quantification
NIST	National Institute of Standards and Technology
RfD	Reference Dose
RSD	Relative Standard Deviation
SD	Standard Deviation
SRM	Standard Reference Material
STD	Standard mode

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TF Translocation Factor
THQ Target Hazard Quotient

Introduction

It is well known that the occurrence, as well as the relative abundance of native perennial plants correlate with their physiological and ecological tolerances, provided important information about the environment pollution degree, which doubtless having obvious implications in human health (Radulescu et al. 2013; Zacarias et al. 2012; Zhu et al. 2018). This means that native plants (considered by the specialists being in category of wild weeds) are widely used for ecological restoration (Gerhart et al. 2004; Waring and Running 2007; Lal 2016), in soil phytoremediation processes, especially in agriculture (Jan et al. 2016; Tangahu et al. 2011), as well as in traditional medicine (Radulescu et al. 2013).

The rural population of many countries considers the perennial plants as an alternative for different diseases treatment due to their psychological properties. Very often, the peoples ignore the potential risks in using these plants, by the lack of information relating to their metal-accumulation potential (Adriano 2001; Buruleanu et al. 2018, 2019). Heavy metals are chemical elements that naturally belong to ecological systems (i.e., atmospheric, continental, limnic and marine systems), but become pollutants once extracted (Pehoiu et al. 2019; Nichols et al. 2009; Kabata-Pendias and Pendias 2001; Bradl 2005). This phenomenon has led to entrances from anthropogenic sources far exceeding the contributions from natural sources. Each metal can be characterized by an anthropogenic enrichment factor, which is the percentage associated with anthropogenic sources in the total annual emissions of a metal. This factor is 97% for Pb, 89% for Cd, 72% for Zn, 66% for Hg, and 12% for Mg (Postolache and Postolache 2000). Heavy metals are a major category of stable toxic pollutants, are not biodegradable, have a weak mobility, and therefore persist in soil for a long period of time. Metals are neither created nor destroyed by biological or chemical processes. These processes can only determine the transition of metal in various chemical species (by valence changing) or the conversion between inorganic and organic forms. One of the main problems associated with persistence, is the bioaccumulation and bioamplification potential of heavy metals, which can lead to increasing the pollutant persistence in the soil, with long-term risks at ecological systems level. The mobility of metals is directly influenced by their chemical speciation (VanBriesen et al. 2010; Yang et al. 2016; Made et al. 2016; Radulescu et al. 2014), which refers to the appearance of metals in various chemical forms (i.e., free metal ions, metal complexes dissolved in solutions and adsorbed on solid surfaces or metal species that coprecipitated in their own solids or other metals with much higher concentrations). At ground level, the heavy metals are distributed, according to the chemical state, through surface flows, hydrological infiltration flows to groundwater and flows to plants and organisms that can take on trophic way, different substances from the soil. The metals transfer from the soil to the plants is influenced by a variety of soil parameters, such as: pH and Eh values, fine grain fraction (<0.02 mm), organic matter, oxides and hydroxides, especially Fe, Mn, Al, microorganisms (Radulescu et al. 2013, b; Barbes et al. 2014). The concentration of metals in soil and their bioavailability, as well, will also depend by the other physicochemical soil properties (Pehoiu et al. 2019), such as: the chemical nature of metal exchange sites in organic and inorganic matrices, or the affinity for anionic ligands from the water present in soil pores, hydrological regime, climatic conditions, nutrient content and the concentration of other metals. Finally, the transfer of the metals in the trophic levels succession has a strong significance for peoples, due to the need for understanding the principles of heavy metals transfer and bioaccumulation in the trophic network, alongside the determination of toxicity and effects, as well. Conventionally, depending on the value of the transfer factor, the metals can be transferred into the plants by accumulation (factor < 1 by decreasing the concentration), with keeping the concentration, or by concentrating (factor > 1). The bioaccumulation process is not specific to all plants (Radulescu et al. 2010a, 2010b), the causes being represented by the differences that occur between the chemical behavior of metals at the cellular level, through biochemical processes.

The main impact on the environment in the mining industry from Banat Region (Romania) derives from tailings ponds and tailings dumps, as well as, from processing plants. As a result, throughout the time, the uncontrolled flow of heavy and radioactive metals into the biosphere has increased. Incorporating into trophic circuits, in inadmissible quantities caused different diseases to humans and animals from Banat region.

In Romania, the wild plants which grow on poisonous tailings dump and are used by the locals are still a sad reality, being used for a long period of time for medical purposes and fresh food, as well. Despite the close of most of the mines in Romania, these plants are at a higher risk of being contaminated with heavy metals. Through the proliferation of herbals, there is an urgent need to assess the extent of exposure to heavy metals as a result of the usage of these herbal medicines. To achieve this goal, the levels of Pb, Cd, Cu, Cr, Ni, Mn and Zn in different wild plants in Romania were determined and few indicators (i.e., transfer factor, translocation factor, estimated daily intakes, carciogenic risk for lead exposure, health risk index, and cumulative health risk) were calculated.

The plant species evaluated in this study are wild perennial plants that are frequently consumed or used in traditional medicine by the local people from the mining Banat Region (Romania). On the other hand, these plants have been studied to have an idea about the intensity of environmental pollution with heavy metals in uranium mining region. To the best of our knowledge, the heavy metal concentration in plant tissues of *Ranunculus ficaria, Plantago major, Taraxacum officinale*, and *Achillea millefolium,* collected from one of polluted and radioactive area of Romania, not been previously reported by any research group. Therefore, the data presented regarding the metal content of these plants collected from uranium dumps of Banat Area, Romania could be assumed as the first record for the literature. On the other hand, in addition to evaluates the level of environmental pollution in Banat area, the selected plants are also examined to determine the Estimated Daily Intakes (EDI), Health Risk Index (HRI) and Cumulative Health Risk (T_{THQ}) values, and it is aimed to reach a judgment about whether their consumption is risky or not in terms of human health.

Materials and methods

Site description

The Banat Region is part of the Carpathian Mountains developed on the orogenic Alpine of the Western Carpathians Mountains, the subdivision of the plateau and limestone mountains, where the karstic relief is predominant (Artugyan 2014). Local conditions allow the existence of original vegetation. Thus, besides forests of beech, spruce, fir, and oak, there are populations of hazelnut, karst-tree forests, meridional types, in which predominate the *Syringa vulgaris*, *Cotinus coggygria, Fraxinus ornus* as well as several native perennial plants such as *Ranunculus ficaria, Plantago major, Taraxacum officinale, Achillea millefolium* and so on (Fig. 1).

Site geology

The Paleozoic-Mesozoic formations of the area which belongs to geological structure of the Southern Carpathians are arranged over the crystalline foundation of the Getic Canvas (Bucur 1997). The geological structures of site include several ages of paleographic evolution (Fig. 2) (i.e., Carboniferous, Permian, Triassic, Jurassic, and Cretaceous) (Geological Institute of Romania 2020; Artugyan 2015).

The Carboniferous stage, as the first pre-alpine coating, overlaps the crystalline schists and it is highlighted by a complex structure formed by: conglomerates, dark micaceous sandstones with intercalations of clays and coal schists and layers (Geological Institute of Romania 2020; Artugyan 2015). The Permian is the next stage in the sedimentation process above the Carboniferous stage and includes deposits of slate black schists, with intercalations of sandstones and microconglomerates, tuffs, sandstones, and clays (Geological Institute of Romania 2020; Artugyan 2015). Triassic, Jurassic and Cretaceous stages were characterized by favorable conditions for the development of carbonate and silicate deposits (i.e. limestones, quartzites, granite) (Geological Institute of Romania 2020; Artugyan 2015). As can be seen in Fig. 2, the area is characterized by the presence of limestones, quartzites, granite (i.e. banatitic granite) with intercalations of sandstones, clays and coal.

Materials

All chemical reagents were of analytical grade. Distilled deionized water (Milli-Q Water System Millipore, USA) was used throughout. Also, hydrogen peroxide and nitric acid (high purity, Merck) was used for the blank preparation (1% nitric acid) and digestion process as well.

Since ancient times, native plants have been used in Romania in traditional medicine. Even today in rural areas, these plants are being used in herbal treatments

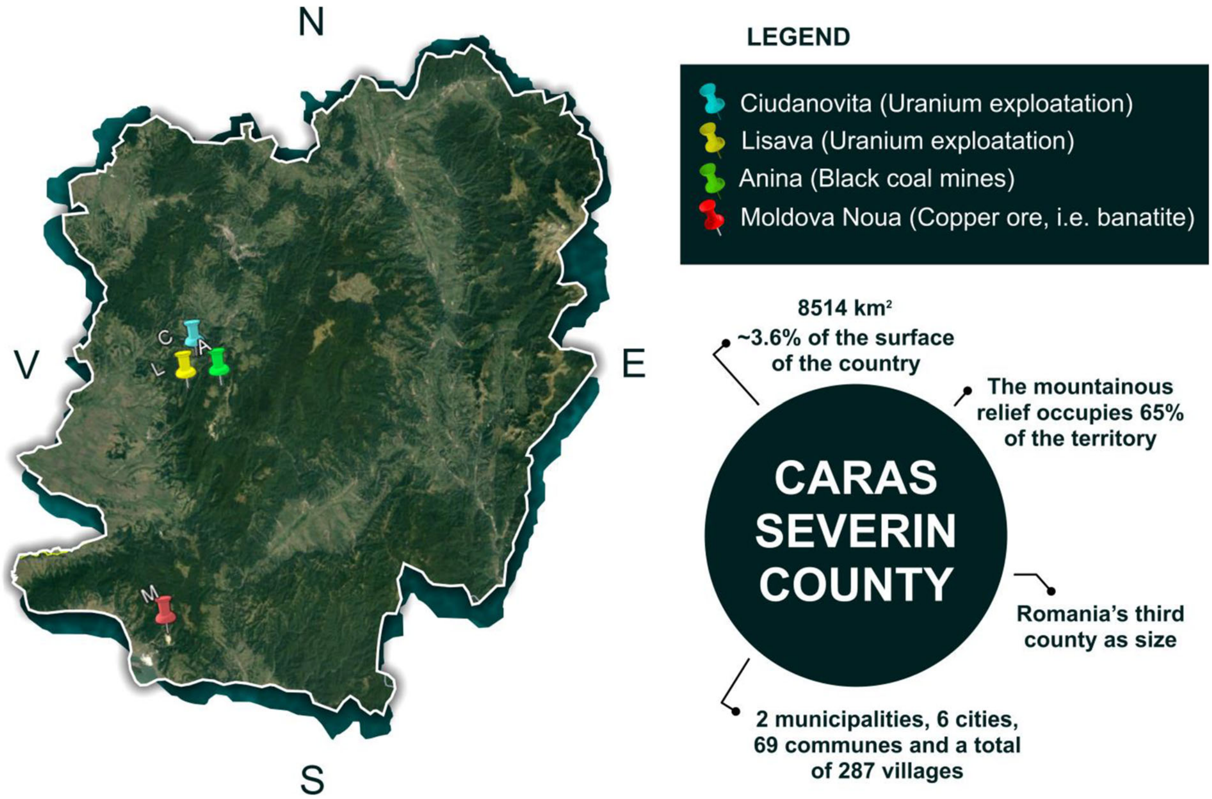

Fig. 1 Site description

against different illness, and some even in nutrition. Among these plants, in Banat Region of Romania, *Plantago major* (*P. major*), commonly known as great plantain (Table 1), is a widespread used medicinal plant from the *Plantaginaceae* family, due to the high content in volatile compounds, triterpenoids, phenolic acids and flavonoids. *P. major* is prescribed in various forms by the rural peoples, but mainly as decoction, syrup, liniment, gargle, or even as drops for eyes and nose for different illness.

Another common medicinal plants, is *Taraxacum officinale*, also known as dandelion or lettuce (Table 1), a plant that belongs to the family *Asteraceae*. The plant has a slightly aromatic smell and when ingested, a bitter taste. For therapeutic purposes, the roots, leaves and flowers of dandelion are used. The chemical substances present in high amounts in the composition of the plant are: caffeic acid, inulin, apigenol, luteolin, taraxacozide, taraxasterol, stigmasterol, sitosterol, and tetrahydroidentine B (Lis and Olas 2019). The dandelion exhibits anti-inflammatory, antiseptic, analgesic, tonic, diuretic, digestive, relaxing, sedative, purifying, healing and immunostimulatory properties. Dandelion can be used for therapeutic purposes as infusion, decoction, extract for different illness, and even as ingredient in salads (Lis and Olas 2019). *Ranunculus ficaria* (Table 1) is a native plant identified in two investigated sites from Banat Region, i.e., Lisava (former uranium extraction) and Anina (active black charcoal mines). The old, traditional name of *R. ficaria* is pilework and comes from the oily taste, persistent after consumption. *Ranunculus ficaria* contains vitamins C and E, calcium, potassium, folic acid and dietary fiber which helps to reduce cholesterol levels and improves circulation (Jaric et al. 2007). In traditional medicine, from ancient times, it is known that the juice obtained by boiling the pilework is an excellent treatment against hemorrhoids (Jaric et al. 2007). The peoples from Banat Region crush the leaves in a stone mortar and mix them with lard, thus obtaining rustic ointment which is also used for hemorrhoids treatment (Hadaruga 2012). For therapeutic purposes,

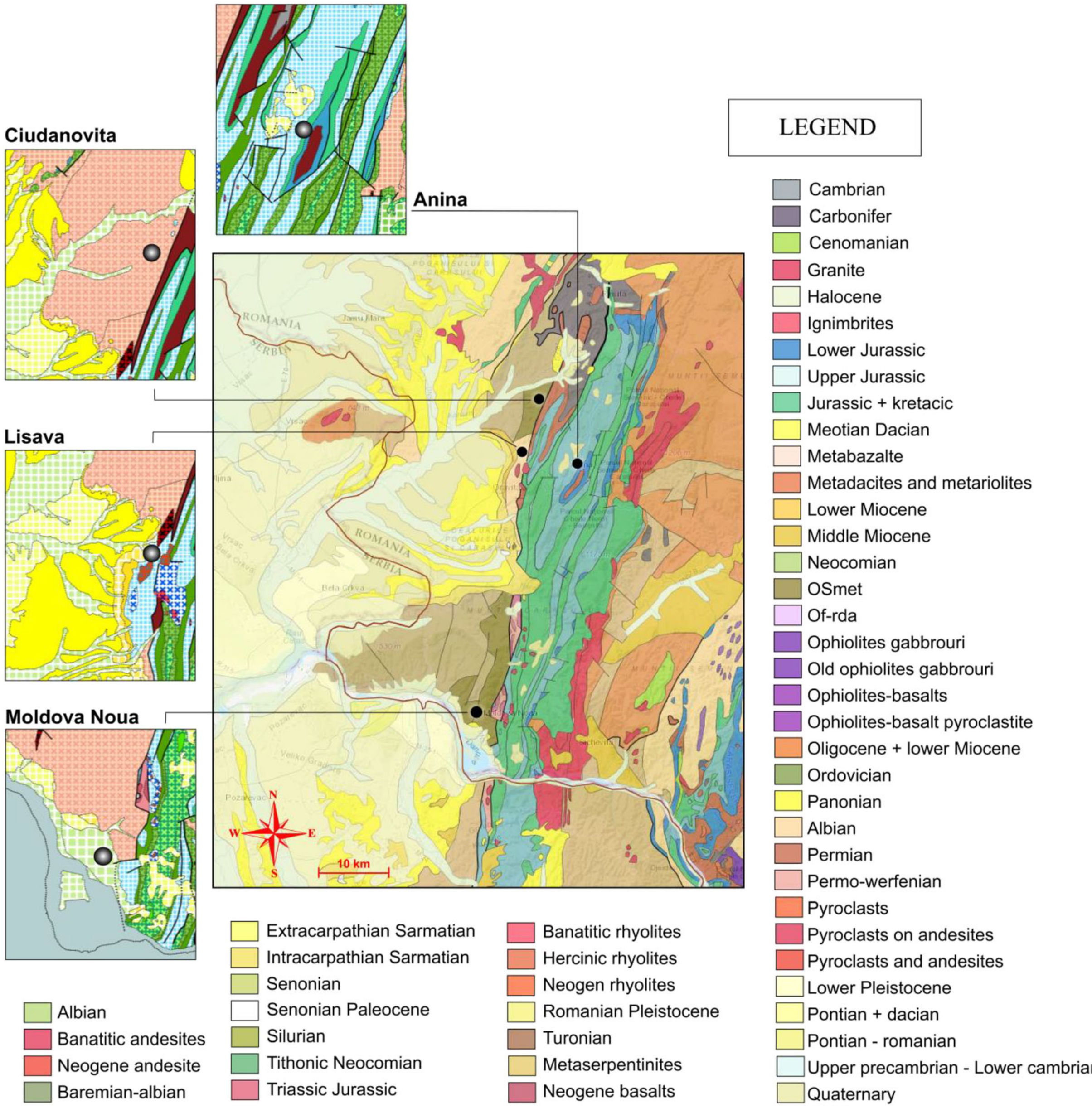

Fig. 2 Site geology

this plant is used as tea, extract, tincture against different diseases related to impure skin (i.e., acne, irritated skin), as well as ingredient for salads.

Achillea millefolium, commonly known as milfoil (Table 1), is a perennial plant from *Asteraceae* family, which was identified in Cidanovita (former uranium mine) and Moldova Noua (active copper extraction), as well. Its astringent effect is due to the tannin, an active component of this plant. The flowers of *Achillea millefolium* contain essential oil, composed of azulene and achilleinic lactone, with anti-inflammatory effect, tannins, anti-inflammatory flavonoids, alkaloids, active ingredients, such as azulene, cineole, etc. (Arias-Duran et al. 2020). People from investigated sites use this plant as tea, infusion, tincture, and cream with excellent anti-inflammatory, astringent and healing properties in case of gingivitis, digestive cramps, respiratory and urinary tract infections (Arias-Duran et al. 2020). The achilein and flavonoid agents are used as hemostatic for internal and external bleedings. Most probably the flavonoids

Table 1 Correspondence between collecting site, sample type and sample codes

Site	Sample type	Sample code
Lisava	*Ranunculus ficaria* - flowers	RfL_1f
	Ranunculus ficaria - leaves	RfL_1l
	Ranunculus ficaria - roots	RfL_1r
	Taraxacum officinale - flowers	ToL_2f
	Taraxacum officinale - leaves	ToL_2l
	Taraxacum officinale - roots	ToL_2r
	Plantago major - leaves	PmL_3l
	Plantago major - roots	PmL_3r
Ciudanovita	*Achillea millefolium* - flowers	AmC_1f
	Achillea millefolium - stem and leaves	AmC_1l
	Achillea millefolium - roots	AmC_1r
	Taraxacum officinale - flowers	ToC_2f
	Taraxacum officinale - leaves	ToC_2l
	Taraxacum officinale - roots	ToC_2r
	Plantago major - leaves	PmC_3l
	Plantago major - roots	PmC_3r
Moldova Noua	*Achillea millefolium* - flowers	AmM_1l
	Achillea millefolium - stem and leaves	AmM_1f
	Achillea millefolium - roots	AmM_1r
	Plantago major - leaves	PmM_2l
	Plantago major - roots	PmM_2r
	Taraxacum officinale - flowers	ToM_3f
	Taraxacum officinale - leaves	ToM_3l
	Taraxacum officinale - roots	ToM_3r
Anina	*Ranunculus ficaria* - flowers	RfA_1f
	Ranunculus ficaria - leaves	RfA_1l
	Ranunculus ficaria - roots	RfA_1r
	Plantago major - leaves	PmA_2l
	Plantago major - roots	PmA_2r
	Taraxacum officinale - flowers	ToA_3f
	Taraxacum officinale - leaves	ToA_3l
	Taraxacum officinale - roots	ToA_3r

are responsible for its antispasmodic effect, as well (Arias-Duran et al. 2020).

Sampling procedure and sample preparation

Plant samples were collected according to Codex Methods of Sampling (Food and Agriculture Organization of United Nations – FAO 2004) from the same tailing dumps described in previous research: for about 8 weeks, were collected 6 samples/week from each three selected areas of studied sites (i.e. 6 samples × 3 areas × 8 weeks = 144 samples × 4 sites, resulting a total of 576 plant samples) (Pehoiu et al. 2019).

The collected fresh plants were carefully cleaned by soil and vegetal wastes with deionized water. Then, each of plant (Table 1) were separated by root, steam, leaves and flowers (excepting *Plantago major*); the obtained samples were cut in small pieces with a plastic knife and dried at 40 °C for 48 h, until the constant weight. Binder drying system was used in the above mentioned scope. The samples, completely free of moisture, were homogenized by using an agate homogenizer, and finally, dried material was grinded in order to obtain a fine powder. After all the above processes were completed, the samples were collected in polyethylene bottles, which were thoroughly cleaned and not containing moisture, and kept until analysis was performed. Each sample belonging to a certain species of plants was weighed, digested and analyzed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS).

About 400 mg of each powdered plant sample (root, leaf and flowers from each plant) were digested in Teflon vessels with 1 mL hydrogen peroxide (31%, high purity) and 9 mL nitric acid (65%, high purity). The TOPwave microwave-assisted pressure digestion system (Analytik Jena, Germany) was used. After digestion process, the PTFE-TFM vessels with samples were cooled for one hour, and then the solutions were transferred with distilled water to 25 mL volumetric flasks. Finally, the clear solution samples were analyzed by ICP-MS technique.

Inductively coupled plasma – Mass spectrometry

The elemental content (i.e., Cr, Mn, Ni, Cu, Zn, Cd, and Pb) of the samples were performed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) using iCAP™ Qc device (Thermo Scientific, Germany) with the parameters presented in Table 2. The measurements were achieved in triplicate in the standard mode (STD), using the Qtegra Intelligent Scientific Data Solution. The relative standard deviation (RSD) values were less than 10%; the data were expressed as mg·kg^{-1} dried weight (d.w.) material.

The quantification of this technique was performed by a standard curve procedure. Metals calibration curves showed good linearity over the concentration range (0.1

Table 2 Instrumental information and data acquisition parameters of iCAP Qc mass spectrometer

Data acquisition parameters quantitative mode		*Sensitivity [kcps·µg^{-1}·L]*	
Measuring mode	Standard (STD)	^{7}Li	50
Point per peak	1	^{59}Co	100
Integration time	3000 ms	^{115}In	220
Replicates	3	^{238}U	300
Instrumental Parameters		*Detection Limits [ng·L^{-1}]*	
		^{9}Be	<0.5
Plasma Power	1548.6 W	^{115}In	<0.1
Nebulizer Ar flow	1 L·min^{-1}	^{209}Bi	<0.1
Plasma Ar flow	10.75 L·min^{-1}	*Oxides [%]*	
Sample uptake rate	0.4 mL·min^{-1}	CeO/Ce	<2.00

to 10.0 mg·L^{-1}), with R^2 correlation coefficients in the range of 0.997 to 0.999. The analytical curves for each analyzed elements were prepared using a stock standard solutions (Merck). The limits of detection (LODs) and limits of quantitation (LOQs) of analyzed elements were established using the calibration data. Standard reference material (i.e. NIST SRM 1515 Apple leaves) was used to verify the accuracy and traceability of the method (Table 3). Accuracy and precision in the ranges of 94–107% and 1–8% were considered sufficient, respectively. Recovery rates and analytical outputs of the reference material are given in Table 3.

Health risk assessment

Transfer factor (BaF), well known as bioaccumulation factor, is an indicator of metal transfer from soil to plants. In fact, this factor represents the ratio between the metal content in plant parts and the metal content in soil sample: $BaF = \frac{C_{plant}}{C_{soil}}$ (Dulama et al. 2012; Radulescu et al. 2013c). The metals transfer process from soil to plants is very important for human health due to the fact that it can explain the risks of human exposure at contaminated soil (Papaioannou et al. 2018).

Translocation factor (TF) can be calculated using the formula: $TF = \frac{C_{tissue}}{C_{root}}$. The translocation represents the ability of plant to distribute different substances (including metals), across the plant tissues. Both factors (BaF and TF) were usually used to evaluate the phytoremediation potential of plants (Ganeshkumar et al. 2019; Wang et al. 2019; Tang et al. 2019).

Estimated daily intake (EDI) represents the estimation of the average of the metals ingested daily into the body system of a consumer. This parameter does not take into account the ejected metals due to the metabolic processes. In this study, EDI was calculated using the following equation / formula

$$EDI = C_{plant} \times I$$

where:

- EDI = Estimated daily intake [mg·day^{-1}];
- C_{plant} = metal content in plant [mg·kg^{-1} d.w.];
- I = average adult daily intake rate [kg·day^{-1}]; for this study it was considered a consumption of 3 tea cups per day, and for each cup approximately 2 g of plant is used (i.e., in this case I = 0.006 kg·day^{-1}).

Carcinogenic risk (CR) was used to estimate the probability to develop cancer as a consequence of exposure to Pb and As (Atique Ullah et al. 2017). Due to the fact that in this study the As content was not determined, the carcinogenic risk (CR) was calculated only for Pb. In this respect, according to US EPA (U.S. Environmental Protection Agency – Integrated Risk Information System, Lead and compounds (inorganic)) which establish the acceptable risk levels between 10^{-6} and 10^{-4} and using the cancer slope factor for Pb (CSF_{Pb} = 0.0085 mg^{-1} kg day), the CR_{Pb} was calculated by the following formula: $CR = CSF \times EDI$(Atique Ullah et al. 2017).

Daily intake metals (DIM) represents the ratio between EDI and body mass (Khan et al. 2009; Likuku and Obuseng 2015; Georgescu et al. 2017):

$$DIM = \frac{C_{plant} \times I}{BM}$$

where:

- DIM = daily intake metals [mg·kg^{-1}·day^{-1}];
- BM = body mass [kg]; for this study it was considered to be 70 kg.

The **health risk index (HRI)** represents the evaluation of health risks induced by the consumption of contaminated teas. HRI can be estimated as the ratio

Table 3 Analytical performance of ICP-MS method

Element	SRM 1515 Apple leaves (n = 5) Mean ± SD [mg·kg^{-1}]		LOD [μg·kg^{-1}]	LOQ [μg·kg^{-1}]	R^2
	Certified values	Measured values			
Cr	0.300 ± 0.000	0.311 ± 0.032	1.500	2.139	0.998
Mn	54.100 ± 1.100	56.700 ± 2.120	0.485	0.564	0.997
Ni	0.936 ± 0.094	0.906 ± 0.072	0.730	0.800	0.999
Cu	5.690 ± 0.130	5.716 ± 0.237	1.198	1.476	0.999
Zn	12.450 ± 0.430	12.512 ± 0.685	8.922	9.349	0.999
Cd	0.013 ± 0.002	0.020 ± 0.009	0.134	0.150	0.998
Pb	0.470 ± 0.024	0.481 ± 0.085	1.235	1.319	0.999

between DIM and the oral reference dose (Likuku and Obuseng 2015):

$$HRI = \frac{DIM}{RfD}$$

where:

– HRI = health risk index;
– RfD = oral reference dose [mg·kg^{-1}·day^{-1}].

In this research were taken into account the RfD values shown in Table 4:

HRI is also known as **target hazard quotient (THQ)**. It is used to estimate the potential health effects expected as a consequence of exposure / ingestion and to evaluate the adverse effects of tea consumption (Atique Ullah et al. 2017). If the THQ value is less than 1, then no adverse health effects are expected. If the value is higher than 1 then, some protective measurements must be taken because there is a potential health risk. If peoples are exposed to more pollutants in the same time, the resulted effects are the sum of individual effects or more (**cumulative health risk**$T_{THQ} = \sum_{i=1}^{n} THQ_i$) (Atique Ullah et al. 2017).

Statistical analysis

All statistical analyses were achieved using IBM SPSS Statistics. In this regards, determination of average values and standard deviation, as well as, principal component analysis (PCA) were performed. Two principal components were confirmed through PCA graphic representation by Varimax method (axis rotation) of health risk index values (Radulescu et al. 2019).

Results and discussion

In the previous studies of authors (Pehoiu et al. 2019; Radulescu et al. 2010a, 2010b; Radulescu et al. 2013a), it was highlighted that the growth native plants, under natural conditions, increases the pH of the rhizosphere. Further, our studies have shown that both changes in pH values and carbonate dissolution can mobilize heavy metals, such as Pb, Cu and Mn, into the rhizosphere and cause subsequent accumulation in the leaves and even flowers. At the same time, acidification of the soil in the root area increases the mobility of Zn and Cu in native plants, being accumulated in root in appreciable quantities and then translocated in leaves, respectively. The first part of this research, published by the authors

Table 4 RfD values for analyzed metals (Likuku and Obuseng 2015; Atique Ullah et al. 2017; U.S. Environmental Protection Agency – Integrated Risk Information System (IRIS), Cr(VI); Cr(III); Mn; Ni; Cu; Zn; Cd; Pb)

	Cr	Mn	Ni	Cu	Zn	Cd	Pb
RfD [mg kg^{-1} day^{-1}]	0.003[a] 1[b]	0.140	0.020	0.040	0.300	0.001	0.035

[a] *value for Chromium (VI);* [b] *value for Chromium (III)*

(Pehoiu et al. 2019), mentioned that the same cause of the lowering of pH is attributed to the increase of Cd mobility. Comparative studies (Prasad 1994; Radulescu et al. 2010a; Radulescu et al. 2013; Radulescu et al. 2013c) between the mechanisms of metal uptake by hyperaccumulator and non-hyperaccumulator native plants, related to changes of pH and redox potential in soil, indicate that for non-hyperaccumulators the nitrogen forms taken over are responsible for changes of pH (i.e. acidification), while for other hyperaccumulators, as the release of chelating agents. At the interface between root and soil, the roots eliminate different excretion products such as oxalic, acetic, fumaric, citric, tartaric, uronic acids and polysaccharides which lead to the formation of different complexes with metal ions, organometallic substances, named chelates (Radulescu et al. 2013). Finally, the plants take over the metals dissolved in soil solution, both in ionic and complexed forms.

The plant's capacity to take over the metals from soil was assessed by the ratio from element concentration in plant and element concentration in soil named bioaccumulation factor (BaF). It is well known that several elements such as, Br, Ca, B, Cs, and Rb are easy accumulated in plants, while other metals Ba, Ti, Zr, Sc, Bi, Ga, Fe, and Se are less available for accumulation, but these aspects can be changed according to the particularities of the soil-plant system (Prasad 1994; Chen et al. 2003). According to Yoshida et al. (1998), the concentration of metals such as Zn, Cd, Cu, Cs, and Rb in a pine forest in Japan was higher in mushrooms than in plants in the same area, while the concentration of Ca and Sr was smaller in mushrooms than in plants. This aspect can be explained by the type of bioaccumulation process, which can be passive or active (McBride 1994). According to Kabata-Pendias and Pendias (2001) passive absorption can be defined by diffusion of ions from the soil solution into the root endoderm, while active absorption is realized at the expense of energy, against the concentration gradient, with remark that the take-over mechanisms, passive or active, are specific to each chemical element. With this respect, the passive take-up path is specifically absorbed for the metals Pb and Ni, while the active absorption is mainly for Cu and Zn (Table 5). On the other hand, the mechanisms for chemical elements accumulation involve the carrying out of processes, such as root cation exchange, transport within plant cells (leaves, via stem) and the effects of the rhizosphere (i.e. microorganisms, pH, redox potential, aeration and so on).

Heavy metals transfer and translocation

Lead

The natural Pb concentration in Banat soils is strongly related to the composition of the bedrock, being known that Pb is reported to be the least mobile among the investigated heavy metals such as Cd, Cr, Ni or Cu. In Kabata-Pendias and Pendias (2001) study was highlighted that in podzols or sandy soils, as well as in brown soils from Romania lead content was ranged from 5.00 to 41.00 mg·kg^{-1} d.w., and 8.00 to 20.00 mg·kg^{-1} d.w. respectively. Regarding the Pb values in soils around of mine extractions from Banat Region, reported in past research (Pehoiu et al. 2019), it was concluded that high Pb contamination factor were highlighted in Ciudanovita Area, followed by Lisava, both sites still considered harmful for human daily activities.

In these areas the acidity of soils increase the Pb solubility and this can be the reason that Pb are accumulated and translocated in native plants such as *Plantago major* (roots) and *Taraxacum officinale* (roots and leaves), according to data from Table 5 and Figs. 3 and 4. However, the Pb amounts from *Plantago major* and *Taraxacum officinale* roots were correlated to the Pb content of the sample soils collected from Ciudanovita and Lisava areas (Pehoiu et al. 2019), which indicates its uptake by these native plants. Certain soil and plant factors (e.g., low pH, organic ligands) are known to promote both Pb uptakes by roots and Pb translocation into plant tops. Lead is considered a harmful and non-essential heavy metal for human's health and must be carefully monitored in environment, in foods and medicinal plants.

Copper

The behavior of Cu in soils is due to the chelation and complexing reaction. The organic compounds from soil composition (e.g., humic and fulvic acids) have the ability to bind Cu under divalent ions in direct coordination with functional oxygen of the organic substances. This is the reason that in previous research (Pehoiu et al. 2019) was reported high Cu concentrations in Moldova Noua soils (i.e. banatite extraction) and this fact is due to the retention of Cu^{2+} by organic-rich soils correlated consequence of exchange of alkali and alkali earth metal cations (i.e. triple Cu^{2+}, Ca^{2+}, and H^{+} cation exchange)

Table 5 Metals content [mg·kg^{-1} d.w.] in plant samples ($n = 8$) expressed as mean value ± SD, compared with maximum allowed limit in Romanian regulation (Romanian Health Ministry 1998)

Sample		**Elemental content [mg kg^{-1} d.w.]**						
		Cr	**Mn**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
Lisava	**RfL_1f**	3.83 ± 0.14	196.83 ± 8.14	2.83 ± 0.10	8.31 ± 0.32	20.91 ± 0.88	3.41 ± 0.11	11.45 ± 0.45
	RfL_1l	6.19 ± 0.27	451.54 ± 18.55	4.17 ± 0.14	11.29 ± 0.44	23.58 ± 0.97	4.88 ± 0.20	24.40 ± 1.01
	RfL_1r	17.35 ± 0.71	823.89 ± 32.09	6.05 ± 0.22	14.57 ± 0.60	40.00 ± 1.25	5.75 ± 0.25	31.68 ± 1.30
	ToL_2f	1.54 ± 0.05	271.78 ± 11.11	0.95 ± 0.04	7.09 ± 0.29	31.29 ± 1.22	15.13 ± 063	27.31 ± 1.13
	ToL_2l	8.62 ± 0.32	632.93 ± 24.02	5.39 ± 0.22	15.30 ± 0.61	46.50 ± 1.92	19.22 ± 0.80	43.21 ± 1.77
	ToL_2r	36.27 ± 1.43	1017.31 ± 38.97	17.17 ± 0.69	17.79 ± 0.77	48.70 ± 1.99	23.45 ± 0.99	60.98 ± 2.25
	PmL_3l	5.18 ± 0.19	223.10 ± 8.92	13.66 ± 0.56	23.71 ± 0.95	34.00 ± 1.40	4.56 ± 0.20	10.73 ± 0.45
	PmL_3r	82.70 ± 3.35	1476.68 ± 57.66	36.74 ± 1.02	65.75 ± 2.17	81.53 ± 3.33	23.22 ± 0.95	64.53 ± 2.26
Ciudanovita	**AmC_1f**	1.64 ± 0.06	237.40 ± 9.72	2.53 ± 0.09	2.47 ± 0.10	33.70 ± 1.36	4.02 ± 0.17	3.10 ± 0.13
	AmC_1l	4.21 ± 0.18	356.59 ± 13.17	4.92 ± 0.18	3.75 ± 0.15	40.08 ± 1.60	11.59 ± 0.44	4.09 ± 0.16
	AmC_1r	7.14 ± 0.31	824.90 ± 32.00	5.61 ± 0.21	4.54 ± 0.18	51.85 ± 2.12	12.46 ± 0.49	24.07 ± 1.01
	ToC_2f	3.28 ± 0.14	347.96 ± 14.13	6.11 ± 0.26	3.54 ± 0.15	10.56 ± 0.40	7.36 ± 0.30	9.33 ± 0.39
	ToC_2l	11.59 ± 0.44	521.52 ± 20.12	11.74 ± 0.49	9.47 ± 0.33	29.15 ± 1.20	13.34 ± 0.52	12.82 ± 0.55
	ToC_2r	29.67 ± 1.06	1745.61 ± 70.09	27.29 ± 1.15	14.74 ± 0.62	33.36 ± 1.32	18.01 ± 0.72	42.94 ± 1.75
	PmC_3l	6.61 ± 0.25	1427.77 ± 55.92	2.18 ± 0.08	10.88 ± 0.44	36.80 ± 1.25	12.85 ± 0.53	17.49 ± 0.70
	PmC_3r	54.92 ± 2.07	2053.22 ± 82.17	6.16 ± 0.29	19.40 ± 0.81	49.63 ± 2.05	14.61 ± 0.60	32.03 ± 1.30
Moldova Noua	**AmM_1f**	1.97 ± 0.05	309.17 ± 11.06	2.09 ± 0.09	9.32 ± 0.38	43.92 ± 1.82	0.18 ± 0.01	0.59 ± 0.02
	AmM_1l	3.30 ± 0.16	376.71 ± 14.58	2.18 ± 0.10	11.96 ± 0.49	44.48 ± 1.85	0.51 ± 0.02	1.30 ± 0.05
	AmM_1r	9.05 ± 0.32	1240.93 ± 48.88	5.89 ± 0.24	25.75 ± 0.98	72.43 ± 3.01	0.67 ± 0.03	2.63 ± 0.11
	PmM_2l	5.01 ± 0.20	1052.99 ± 39.97	3.39 ± 0.14	10.74 ± 0.40	23.36 ± 0.99	0.87 ± 0.04	1.95 ± 0.07
	PmM_2r	55.32 ± 2.18	1503.38 ± 42.05	6.48 ± 0.27	12.12 ± 0.51	34.36 ± 1.41	1.21 ± 0.05	2.35 ± 0.10
	ToM_3f	3.45 ± 0.13	794.78 ± 60.03	11.37 ± 0.47	12.99 ± 0.55	32.68 ± 1.35	0.75 ± 0.03	0.74 ± 0.03
	ToM_3l	3.62 ± 0.14	856.92 ± 32.77	13.47 ± 0.56	24.98 ± 1.02	36.57 ± 1.52	1.36 ± 0.06	1.41 ± 0.05
	ToM_3r	14.22 ± 0.55	1093.45 ± 35.35	14.48 ± 0.58	31.00 ± 1.22	59.83 ± 2.50	1.86 ± 0.08	7.32 ± 0.30
Anina	**RfA_1f**	1.55 ± 0.07	392.60 ± 45.11	1.86 ± 0.09	9.15 ± 0.38	24.10 ± 1.00	0.45 ± 0.02	1.32 ± 0.05
	RfA_1l	14.36 ± 0.54	810.10 ± 16.25	11.30 ± 0.44	10.57 ± 0.42	39.00 ± 1.62	1.62 ± 0.07	2.95 ± 0.14
	RfA_1r	23.04 ± 0.94	1030.14 ± 30.24	17.42 ± 0.71	12.48 ± 0.52	76.52 ± 3.18	2.88 ± 0.11	3.38 ± 0.15
	PmA_2l	5.41 ± 0.22	474.77 ± 41.15	3.81 ± 0.15	10.00 ± 0.44	37.41 ± 1.45	1.42 ± 0.07	1.17 ± 0.05
	PmA_2r	22.53 ± 0.91	1413.29 ± 17.84	15.30 ± 0.62	29.01 ± 1.22	66.12 ± 2.38	2.06 ± 0.09	3.31 ± 0.13
	ToA_3f	4.64 ± 0.18	710.44 ± 55.05	2.75 ± 0.11	3.77 ± 0.15	34.24 ± 1.40	0.43 ± 0.03	1.82 ± 0.06
	ToA_3l	6.88 ± 0.26	867.05 ± 28.26	3.08 ± 0.13	5.99 ± 0.25	42.93 ± 1.70	1.48 ± 0.06	2.13 ± 0.08
	ToA_3r	13.53 ± 0.49	1278.99 ± 52.77	14.33 ± 0.58	6.07 ± 0.22	87.98 ± 3.60	2.53 ± 0.10	4.14 ± 0.15
Maximum allowed limit[a]		na[b]	na[b]	na[b]	50	50	0.5	5

[a] *Maximum allowed limit according to Romanian Order no. 975/16.12.1998 – Hygienic and sanitary norms for food (tea plants);* [b] *in the order mentioned above are not available the maximum allowed limits for Cr, Mn and Ni*

and pH of soil, as well. It is well-recognized (Pehoiu et al. 2019) that copper is naturally abundant in soils, as free and complexed ions, however this metal is one of the least mobile heavy metals in soil. This can be the explication that in the area with a large copper extraction and massive pollution (i.e. Moldova Noua, near Danube River and at the border with Serbia), only in the roots of *Taraxacum officinale* (ToM_3r) was obtained a high concentration of Cu, 31.00 ± 1.22 mg·kg^{-1} d.w. (Table 5), but this value not exceed the maximum allowed limit according to Romanian legislation. It is important to specify that the samples were collected

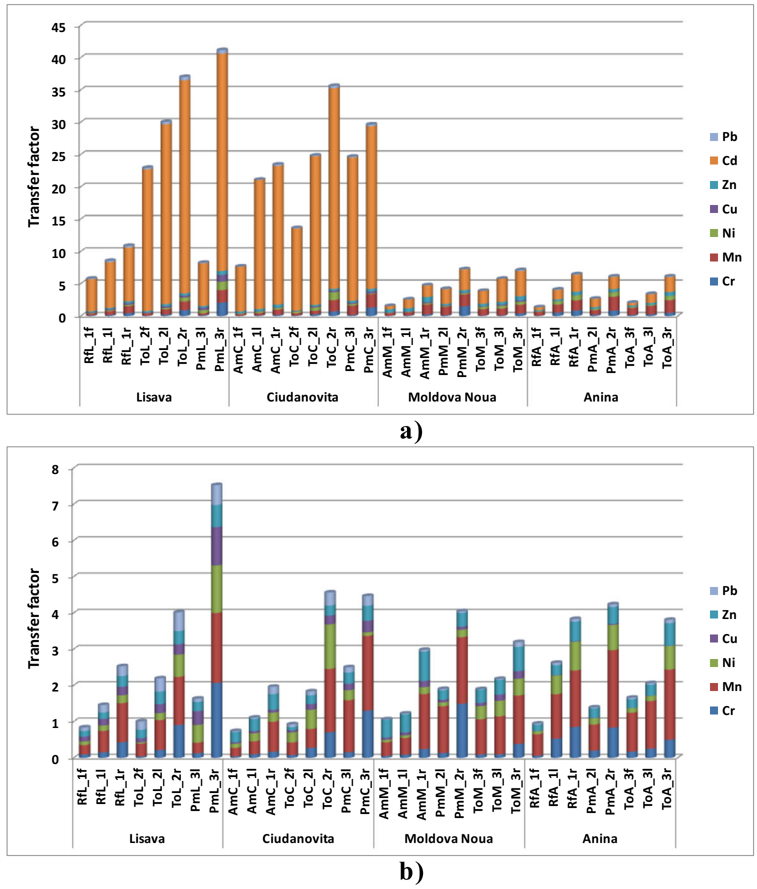

Fig. 3 Transfer of metals from soil to plant parts: a) transfer of Pb, Cd, Zn, Cu, Ni, Mn and Cr; b) transfer of Pb, Zn, Cu, Ni, Mn and Cr

from five points from each tailing dump around the copper extraction (i.e., five dumps).

Surprising in this study is the fact that another perennial plant from a mining area under conservation (i.e., Lisava uranium mine), namely *Plantago major* accumulated a large amount of copper from the soil in the roots (mainly under complexed forms), the obtained value 65.75 ± 2.17 mg·kg^{-1} d.w. far exceeded the permissible limit according to Romanian legislation (Table 5). About one-third of this value, 23.71 ± 0.95 mg·kg^{-1} d.w. (Table 5 and Figs. 3 and 4) was obtained in leaves sample, which means that after the root has accumulated copper, there has been a translocation

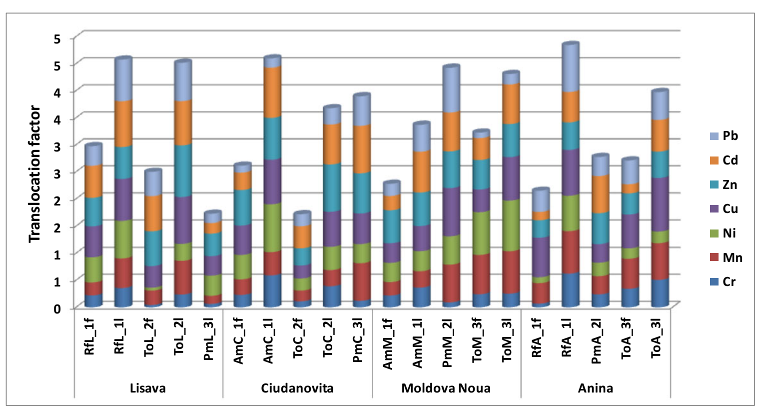

Fig. 4 Translocation of metals from root in plant tissues

of metal ions to the tissues and organs at the level of the leaves, where they are then stored, accumulated and immobilized.

The mobility of metals in the process of displacement in *Plantago major* leaves is influenced by a number of factors such as pH, oxidation-reduction state, hydrolysis, formation of insoluble salts, all factors being a consequence of uranium tailing dumps from investigated area. However, the accumulation and translocation of metal ions is recorded in different structures of the plants, the quantitative differentiation being variable depending on the type of metal ion, plant species, and the stage of development and pedoclimatic conditions.

Therefore, the distribution of Cu within native plants is highly variable (Figs. 3 and 4); within root plants, copper is associated mainly with cell walls and is less mobile. The highest concentrations of Cu in leaves or flowers are always in intensive growth phases of plants (Figs. 3 and 4). In this regard, from Table 5 and Figs. 3 and 4, it can be easy observed that in leaves and flowers of *Taraxacum officinale* (i.e. ToC_2l and ToC_2f from Ciudanovita; ToA_3l and Toa_2f from Anina; ToL_2l and ToL_2f from Lisava) were translocated and stored high quantities of copper, although in roots the copper contents (14.74 ± 0.62 mg·kg^{-1} d.w.) not exceed the maximum allowed limit according to Romanian regulation (i.e. 50 mg·kg^{-1} d.w.). However, copper is a toxic metal for plants when is in high concentrations. The usual symptoms of copper toxicity in plants, due to accumulation process, were observed by malformation of roots, Cu-induced chlorosis and even inhibition of photosynthetic processes. All these symptoms represent a real risk for human health.

Zinc

In previous research (Pehoiu et al. 2019) were reported high concentrations of Zn in all investigated sites of Banat Region. The solubility of zinc in soils is associated mainly with hydrous oxides of iron, manganese and aluminum, clay minerals and pH. When zinc enters in the layer lattice of phyllosilicate, they become immobile and are less possible to participate to the uptake processes within perennial medicinal plants. On the other hand, Zn can precipitate as hydroxide, carbonate and sulfide compounds or even can be complexed as coordinative compounds (i.e. chelates). Several studies (McBride 1994; Kabata-Pendias and Pendias 2001) reported that Zn absorption within plant roots are achieved in both hydrated Zn and Zn^{2+}, as well as complex ions and Zn-organic chelates.

It is well known that in soil the nucleation process of zinc hydroxide on surface of clay can lead to retention of Zn^{2+}, in strong correlation with pH of soil. Thus, the presence of zinc ions (i.e. solubilization of Zn in order to produce mobile Zn^{2+}) in high quantities in soil is correlated with acid, oxidizing environments, as well as with the presence/amount of aluminum oxides and hydrous iron in soil (Pehoiu et al. 2019). On the other hand, Ca-saturation and P compounds in well-aerated soil with sulphur compounds decrease the solubility and availability of Zn^{2+} in transport and store processes of plants, with a strong Zn deficiency and negative implication within plants growing.

Based on previous data (Pehoiu et al. 2019) and Table 5, the Zn content in roots of *Taraxacum officinale* ranged between 33.36 ± 1.32 mg·kg^{-1} d.w. (ToC_2r) and 87.98 ± 3.60 mg·kg^{-1} d.w. (ToA_3r), higher values, which exceed the maximum allowed limit according to Romanian regulation (i.e., 50 mg·kg^{-1} d.w.), were observed in sites with cooper and coal extraction, from Moldova Noua and Anina, respectively. Instead *Plantago major*, the second perennial plants collected from all investigated sites, accumulated higher amount of Zn (i.e., 81.53 ± 3.33 mg·kg^{-1} d.w. for PmL_3r) in roots samples collected from Lisava (uranium tailing dump), and these value exceed the maximum allowed limit (i.e. 50 mg·kg^{-1} d.w.).

Cadmium

Usually, the abundance of Cd in magmatic and sedimentary rocks does not exceed the average of 0.3 mg·kg^{-1} d.w., instead the cadmium concentration in non-contaminated soils range from about 0.1 to 1.0 mg·kg^{-1}, being concentrated in argillaceous and shale deposits (Page et al. 1987; Ryan et al. 1982). This metal is strongly associated with Zn presence in soil, and due to the well affinity for sulfur, cadmium exhibits a high mobility than zinc in acid soil (i.e., pH 4.5 to 5.5) (Lund et al. 1981). The mobility of Cd^{2+} from soil in plant is determined by two important factors, such as: pH and oxidation potential (Pehoiu et al. 2019). With respect of previous study (Pehoiu et al. 2019) a stronger relationship was observed for Cd with Fe and Mn contents of contaminated soil (i.e., tailing dumps). High concentrations of cadmium were translocated in plant tissues (Fig. 3), especially in leaves.

Manganese

The manganese compounds are very important for soil, being well known for their rapid oxidation and reduction under variable soil environments. In this respect, the Mn that is an essential element for plant nutrition, when it is in low amounts, in different oxidizing conditions may reduce the availability of several other micronutrients even up to the toxicity range, by controlling the behavior of them (Wolnik et al. 1985). On the other hand, Mn has an important effect on the redox and pH regulation of soil. Wolnik et al. (1985), reported that soluble Mn in soil solutions is mainly involved in organic complexing (i.e., fulvic acid, but in the same time, the ions of Mn(II) complexing bounds with this acid are highly ionized). In the polluted soil or tailing dumps as e.g. (Pehoiu et al. 2019), close to the plant roots, the reduction of Mn(IV) forms (e.g., oxides) correlated with weak alkaline pH, and complexing by root exudates can be an important factor in terms of controlling Mn mobility. Starting from this idea, it can be explained why the high concentrations of manganese where found in all rots plant samples (Fig. 3b) and then are translocated among tissue of plants, mainly in stem (Fig. 4). Regarding the passive absorption of Mn from soil to the plant tissues, it is probable to occur due to the high concentrations of free cationic forms (e.g., mainly Mn(II), but not excepting Mn(IV) or Mn(VI)). It should be concluded, that the Mn level in different tissue of perennial plants is not only an effect of plant characteristics (i.e., specie, age, type of tissue etc.) but also of soil properties from sampling area (i.e., pH, compact soil and composition, etc.).

Chromium

As can be seen from the data given in Table 5, the Cr content of analyzed plant tissues of *Ranunculus ficaria* is between 17.35 ± 0.71 and 23.04 ± 0.94 mg·kg^{-1} in root, 6.19 ± 0.27 and 14.36 ± 0.54 mg·kg^{-1} in leaves and 1.55 ± 0.07 and 3.83 ± 0.14 mg·kg^{-1} in flowers. While *Achillea millefolium* had the lowest Cr content in root (i.e., 7.14 ± 0.31 mg·kg^{-1} and 9.05 ± 0.32 mg·kg^{-1}, respectively), it was found that the lowest Cr content in flowers (i.e, 1.64 ± 0.06 mg·kg^{-1} and 1.97 ± 0.05 mg·kg^{-1}). It was found that the Cr content of *Plantago major* was also significantly higher than that of the others three selected species (*Ranunculus ficaria, Taraxacum officinale*, and *Achillea millefolium*) in investigated sites (i.e., Lisava, Ciudanovita, Moldova Noua, and Anina) according to data from Table 5. Elemental analyzes showed that Cr contents of *Taraxacum officinale* was between 13.53 ± 0.49 and 36.27 ± 1.43 mg·kg^{-1} in root, between 3.62 ± 0.14 and 11.59 ± 0.44 mg·kg^{-1} in leaves and 1.54 ± 0.05 and 4.64 ± 0.18 mg·kg^{-1} in flowers. The results obtained from the present study on the Cr content of *Taraxacum officinale* were found to be higher than some literature data (Radulescu et al. 2013; Radulescu et al. 2013b), while for *Achillea millefolium* was slightly high than some previous data (Radulescu et al. 2013).

Nickel

Contrary to the data discussed above, the Ni contents of the *Ranunculus ficaria, Plantago major, Taraxacum officinale,* and *Achillea millefolium* species, obtained by this research were found to be higher in roots than flowers or leaves, as expected (Table 5). However, to the best of our knowledge, previous data reported by authors (Radulescu et al. 2013, Radulescu et al. 2013b) are lower than the Ni concentrations obtained from the current study, according to the Ni content in soil reported by Pehoiu et al. (2019).

It should be highlighted that most of the literature data belongs to perennial plant species collected from forest or rural areas with low pollution. Considering that these four plant species investigated in this study are collected from a mining and radioactive area, this situation is quite thought-provoking.

In the same time, few complex interactions of copper with other metals are well-recognized within plant roots, especially in the uptake-transport processes, with significant effect on human health: Cu-Zn interactions, each of them can inhibited the absorption in plant roots; Cu-Fe interactions is highlighted as an antagonism which can lead a Cu-induced chlorosis in plants; Cu-Cd antagonism and synergism in metal uptake by plant roots; Cu-Mn interactions can be both synergistic and antagonistic in absorption processes at high concentrations of one of the metals; Cu-Ni relationship is intensified at high concentrations of both metals due to association; Cu-Cr antagonism are related to the type of Cr ions (i.e., valence) and may occur within roots and leaves.

Taking in consideration several hypotheses such as, plants behave both as “accumulators” and “excluders” (Sinha et al. 2007), restrict contaminant uptake inside, and do not accumulate trace elements beyond near-term metabolic needs, can be concluded that plants developed a specific process to translocate and store nutrients.

Estimated daily intake and CARCIOGENIC risk

As explained in the above section estimated daily intake (EDI) means the amount of metal to be taken into the body daily depending on the consumption of the plant species investigated in this research. Estimated daily intakes of the determined elements in plants, compared with recommended values or tolerable intake level (TI) and the carcinogenic risk (CR) calculated for Pb exposure (Carrington et al. 2000) are calculated and presented in Table 6. In order to determine EDI values are within the legal limits to be taken in a healthy diet, reference dose values reported by Institute of Medicine (2001), European Food Safety Authority (2011) and U.S. Environmental Protection Agency – Integrated Risk Information System (IRIS) (CASRN 7439-92-1; CASRN 18540-29-9; CASRN 16065-83-1; CASRN 7439-96-5; CASRN Various; CASRN 7440-5–8; CASRN 7440-66-6; CASRN 7440-43-9) , were taken into consideration (Table 6).

The evaluation of the daily metal intake data can be made on element basis, or by considering the plant tissue individually. Both forms of presentation are scientifically satisfying. If an evaluation based on elements is required, it can be stated that none of the studied plant species detected to contain Cu, Zn, and Ni below the reference dose, both for male and female (Table 6). However, other elements (i.e., Mn, Pb, and Cd) were found to be high than the reference dose (both for male and female) in some plant species, especially in roots (Table 6), due to accumulation of these metals from soil. However, it has been determined that the use or consumption of plant roots is not safe from heavy metals presence point of view. Therefore, according to data calculated (Table 6) it can be concluded that only *Achillea millefolium* can be safely used by the peoples (i.e., male and female), excepting the AmM_1r sample collected from Moldova Noua.

In addition, *Taraxacum officinale* are thought to be harmful to health in terms of Cd, Cr, Mn and Pb, heavy metals known to cause serious health problems, with a high carcinogenic risk. Apart from these, plant species and elements of which daily intake indexes exceed the reference dose are as follows: *Ranunculus ficaria* (Cr, Mn, Cd and Pb, in leaves and root samples), *Plantago major* (Cr and Mn in root samples, as well as Cd and Pb in leaves and root samples collected from uranium mining area), *Taraxacum officinale* (Cr, Mn, Cd, and Pb in leaves and root samples collected from Lisava and Ciudanovita sites, as well as Cr and Mn in leaves and root samples collected from Anina and Moldova Noua), and *Achillea millefolium* (Cr, Mn, Cd, and Pb only for root sample collected from Ciudanovita uranium extraction area).

Health risk assessment

Since the health risk assessment value is calculated based on daily metal intake data, in this section, results like the data discussed above were obtained. As a result of the calculations, it was concluded that *Achillea millefolium* did not have a negative effect on human health in terms of all metals examined. However, it was understood that other plant species have high health risk index values for certain metals (Table 7).

In this regard, *Taraxacum officinale* and *Plantago major* stand out with their high health risk indexes. The health risk index values of *Taraxacum officinale* in terms of Cd, were determined to be 1.30, 1.65 and 2.01, for flower, leave and root sample collected from Lisava, and 0.63, 1.14 and 1.54 for the same sample collected from Ciudanovita, respectively. In addition, the health risk index values of *Plantago major* in terms of Cr, Cd and Mn in root samples collected from Cidanovita were calculated as 1.57, 1.25 and 1.26, respectively.

It has been determined that *Taraxacum officinale* and *Plantago major* have high risk index values in terms of heavy metals (Cd, Cr and Mn) that have harmful effects on human health. Additionally, cumulative health risk (T_{THQ}) calculated for plant tissue samples (Table 7) shown that *Taraxacum officinale* and *Plantago major* collected from uranium dumps have a cumulative health risk index higher than 1.0 in terms of Cr, Cd and Mn. However, it is anxious that some plant species pose a risk to human health in terms of heavy metals.

Based on HRI data reported in Table 7, it was drawn the principal component analysis graph (Fig. 5). The collected samples are grouped in 2 clusters: the first cluster contains Lisava and Ciudanovita (both locations were extraction areas of uranium) and the second contains Moldova Noua and Anina (extraction areas of copper and charcoal).

Conclusions

The research presented in this article highlighted the main source of heavy metal contamination (i.e.,

Table 6 Estimated daily intakes (EDI) of the determined elements in plants, compared with recommended values or tolerable intake level (TI) and the carcinogenic risk (CR) calculated for Pb exposure

Samples		Estimated daily intakes (EDI) of elements [mg day^{-1}]							CR_{Pb}
		Cr	Mn	Ni	Cu	Zn	Cd	Pb	
Lisava	**RfL_1f**	0.023	1.181	0.017	0.050	0.125	0.020	0.069	**5.84E-04**
	RfL_1l	**0.037**	**2.709**	0.025	0.068	0.141	**0.029**	0.146	**1.24E-03**
	RfL_1r	**0.104**	**4.943**	0.036	0.087	0.240	**0.034**	0.190	**1.62E-03**
	ToL_2f	0.009	1.631	0.006	0.043	0.188	**0.091**	0.164	**1.39E-03**
	ToL_2l	**0.052**	**3.798**	0.032	0.092	0.279	**0.115**	**0.259**	**2.20E-03**
	ToL_2r	0.218	**6.104**	0.103	0.107	0.292	**0.141**	**0.366**	**3.11E-03**
	PmL_3l	0.031	1.339	0.082	0.142	0.204	**0.027**	0.064	**5.47E-04**
	PmL_3r	**0.496**	**8.860**	0.220	0.395	0.489	**0.139**	**0.387**	**3.29E-03**
Ciudanovita	**AmC_1f**	0.010	1.424	0.015	0.015	0.202	0.024	0.019	**1.58E-04**
	AmC_1l	0.025	2.140	0.030	0.022	0.241	**0.070**	0.025	**2.09E-04**
	AmC_1r	**0.043**	**4.949**	0.034	0.027	0.311	**0.075**	0.144	**1.23E-03**
	ToC_2f	0.020	2.088	0.037	0.021	0.063	**0.044**	0.056	**4.76E-04**
	ToC_2l	**0.070**	**3.129**	0.070	0.057	0.175	**0.080**	0.077	**2.19E-03**
	ToC_2r	**0.178**	**10.474**	0.164	0.088	0.200	**0.108**	**0.258**	**6.54E-04**
	PmC_3l	**0.040**	**8.567**	0.037	0.065	0.221	**0.077**	0.105	**8.92E-04**
	PmC_3r	**0.330**	**12.319**	0.013	0.116	0.298	**0.088**	0.192	**1.63E-03**
Moldova Noua	**AmM_1f**	0.012	1.855	0.013	0.056	0.264	0.001	0.004	3.02E-05
	AmM_1l	0.020	2.260	0.013	0.072	0.267	0.003	0.008	6.65E-05
	AmM_1r	**0.054**	**7.446**	0.035	0.154	0.435	0.004	0.016	**1.34E-04**
	PmM_2l	0.030	**6.318**	0.020	0.064	0.140	0.005	0.012	9.92E-05
	PmM_2r	**0.332**	**9.020**	0.039	0.073	0.206	0.007	0.014	**1.20E-04**
	ToM_3f	0.021	**4.769**	0.068	0.078	0.196	0.005	0.004	3.78E-05
	ToM_3l	0.022	**5.142**	0.081	0.150	0.219	0.008	0.008	7.21E-05
	ToM_3r	**0.085**	**6.561**	0.087	0.186	0.359	0.011	0.044	**3.73E-04**
Anina	**RfA_1f**	0.009	**2.356**	0.011	0.055	0.145	0.003	0.008	6.74E-05
	RfA_1l	**0.086**	**4.861**	0.068	0.063	0.234	0.010	0.018	**1.50E-04**
	RfA_1r	**0.138**	**6.181**	0.105	0.075	0.459	0.017	0.020	**1.73E-04**
	PmA_2l	0.032	**2.849**	0.023	0.060	0.224	0.008	0.007	5.97E-05
	PmA_2r	**0.135**	**8.480**	0.092	0.174	0.397	0.012	0.020	**1.69E-04**
	ToA_3f	0.028	**4.263**	0.016	0.023	0.205	0.003	0.011	9.26E-05
	ToA_3l	**0.041**	**5.202**	0.018	0.036	0.258	0.009	0.013	**1.08E-04**
	ToA_3r	**0.081**	**7.674**	0.086	0.036	0.528	0.015	0.025	**2.11E-04**
Recommended daily intake [mg day^{-1}]	**Male**	0.033	2.3	1.0[a]	0.9	11[b]	0.025[c]	0.25[d]	$10^{-6} – 10^{-4}$ [e]
	Female	0.025	1.8	1.0[a]	0.9	9[b]	0.025[c]	0.25[d]	$10^{-6} – 10^{-4}$ [e]

[a] *For Ni are presented the values for Tolerable Intake Level (TI), not the RDI (Institute of Medicine 2001);* [b] *RDI has no values of zinc requirements for adults; in this Table are presented values for ages 14–18 years (boys and girls) (Institute of Medicine 2001);* [c] *For Cd are presented the values for Tolerable Intake Level (TI), not the RDI, calculated from the tolerable weekly intake (TWI) of 2.5 μg/kg b.m., considering the average body mass = 70 kg (European Food Safety Authority 2011);* [d] *For Pb are presented the values for Tolerable Intake Level (TI), not the RDI, calculated from the tolerable weekly intake (TWI) of 25 μg/kg b.m., considering the average body mass = 70 kg (Carrington 2000);* [e] *The acceptable risk levels for CR_{Pb} (U.S. Environmental Protection Agency – Integrated Risk Information System (IRIS), Lead)*

Table 7 Health risk index (HRI) and cumulative health risk (T_{THQ}) calculated for each plant tissue sample

Sample		HRI							T_{THQ}
		Cr	Mn	Ni	Cu	Zn	Cd	Pb	
Lisava	**RfL_1f**	0.11	0.12	0.01	0.02	0.01	0.29	0.03	0.59
	RfL_1l	0.18	0.28	0.02	0.02	0.01	0.42	0.06	0.98
	RfL_1r	0.50	0.50	0.03	0.03	0.01	0.49	0.08	1.64
	ToL_2f	0.04	0.17	0.00	0.02	0.01	**1.30**	0.07	1.60
	ToL_2l	0.25	0.39	0.02	0.03	0.01	**1.65**	0.11	2.46
	ToL_2r	**1.04**	0.62	0.07	0.04	0.01	**2.01**	0.15	3.94
	PmL_3l	0.15	0.14	0.06	0.05	0.01	0.39	0.03	0.82
	PmL_3r	**2.36**	0.90	0.16	0.14	0.02	**1.99**	0.16	5.74
Ciudanovita	**AmC_1f**	0.05	0.15	0.01	0.01	0.01	0.34	0.01	0.57
	AmC_1l	0.12	0.22	0.02	0.01	0.01	0.99	0.01	1.38
	AmC_1r	0.20	0.51	0.02	0.01	0.01	**1.07**	0.06	1.88
	ToC_2f	0.09	0.21	0.03	0.01	0.00	0.63	0.02	1.00
	ToC_2l	0.33	0.32	0.05	0.02	0.01	**1.14**	0.03	1.90
	ToC_2r	0.85	**1.07**	0.12	0.03	0.01	**1.54**	0.11	3.72
	PmC_3l	0.19	0.87	0.03	0.02	0.01	**1.10**	0.04	2.27
	PmC_3r	**1.57**	**1.26**	0.01	0.04	0.01	**1.25**	0.08	4.22
Moldova Noua	**AmM_1f**	0.06	0.19	0.01	0.02	0.01	0.02	0.00	0.30
	AmM_1l	0.09	0.23	0.01	0.03	0.01	0.04	0.00	0.42
	AmM_1r	0.26	0.76	0.03	0.06	0.02	0.06	0.01	1.18
	PmM_2l	0.14	0.64	0.01	0.02	0.01	0.07	0.00	0.91
	PmM_2r	**1.58**	0.92	0.03	0.03	0.01	0.10	0.01	2.67
	ToM_3f	0.10	0.49	0.05	0.03	0.01	0.06	0.00	0.74
	ToM_3l	0.10	0.52	0.06	0.05	0.01	0.12	0.00	0.87
	ToM_3r	0.41	0.67	0.06	0.07	0.02	0.16	0.02	1.40
Anina	**RfA_1f**	0.04	0.24	0.01	0.02	0.01	0.04	0.00	0.36
	RfA_1l	0.41	0.50	0.05	0.02	0.01	0.14	0.01	1.13
	RfA_1r	0.66	0.63	0.07	0.03	0.02	0.25	0.01	1.67
	PmA_2l	0.15	0.29	0.02	0.02	0.01	0.12	0.00	0.62
	PmA_2r	0.64	0.87	0.07	0.06	0.02	0.18	0.01	1.84
	ToA_3f	0.13	0.43	0.01	0.01	0.01	0.04	0.00	0.64
	ToA_3l	0.20	0.53	0.01	0.01	0.01	0.13	0.01	0.90
	ToA_3r	0.39	0.78	0.06	0.01	0.03	0.22	0.01	1.50

occurrence on tailings dump), the effect on wild plant quality, used for different medical purposes by the locals, as well as adverse effects on human health. It is well known that various abiotic factors influence the availability of metal to plants including pH, temperature, redox potential, cation exchange capacity, and soil/sediment composition. Furthermore, the interactions of soil-plant roots play vital roles in regulating heavy metal accumulation and translocation processes from the tailings to the collected wild plant parts. In this respect, in this research, some plant species are not suitable for use and consumption for humans or medical purposes, but data obtained as a result of elemental analysis of these samples can be an indicator of environmental pollution. The high amounts of Cd, Mn, and Pb, which are heavy metals, in tissues of *Taraxacum officinale* and *Plantago major*, lead to the fact that the ecosystem in which these species are growing should be evaluated by

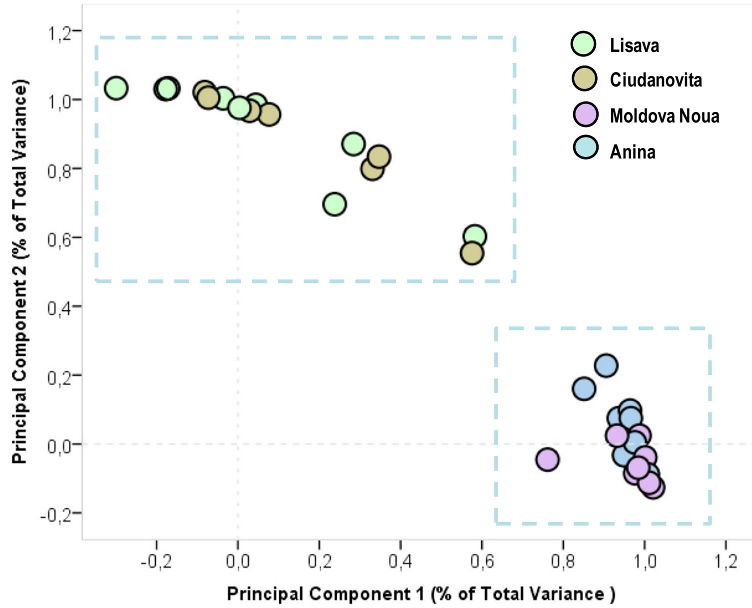

Fig. 5 Principal component analysis of HRI values

the authorities in terms of environmental pollution. On the other hand, as a result of metal intake and health risk index calculations on plant species, it was concluded that *Achillea millefi*ori and *Ranunculus ficaria* can be safely used in terms of all the studied elements. However, *Taraxacum officinale* and *Plantago major* species are thought to pose a risk to human health in terms of Cd, Mn, Pb, and Cr, as well as of other heavy metals. Therefore, the accumulation of metals by both roots and leaves in *T. officinale* and *P. major* is proportional to the metal concentration in the tailings dump (previously values reported by authors). The concentrations of chromium, manganese, cadmium, and lead exceeded their respective maximum permissible daily levels, mainly in roots and leaves for all wild plants collected from both Ciudanovita and Lisava sites.

The findings generally suggest that the use of these plant species for the management of diseases will not cause toxicity in terms of heavy metal and may be beneficial to the users in cases of micronutrient deficiency, as these metals were found to be present in readily bioavailable form.

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