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ORIGINAL PAPER

A new two-step screening method for prospecting of trace element accumulating plants

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Abstract A vulnerable point of the currently used approach to the search for the new species capable of abnormal accumulation (hyperaccumulation) of trace elements is that most studies have been conducted in laboratory conditions and focused on the determination of a limited number of elements. We propose a methodology that enables screening for multi-element accumulating plants. This methodology is based on two analytical steps: a semiquantitative analysis mode by ICP-MS that allows selection of plant samples which are enriched in one or more trace elements, and a quantitative analysis necessary for confirmation of the results derived from the first step. The proposed methodology was tested in the study of 30 plant samples. Ten elements with the highest concentrations obtained in the semiquantitative analyses were determined quantitatively with the following detection limits (in mg/kg): 0.001 for Ag, 0.08 for Ba, 0.002 for Cd, 0.005 for Co, 0.01 for Cr, 0.003 for Cu, 1.4 for Fe, 0.012 for Mn, 0.03 for Ni, 0.006 for Pb, 0.001 for Sc, 0.001 for Tl and 0.06 for Zn. The CRM recovery values obtained were in the range of 80–103 %, and the precision of the measurements (as RSD) was in the range of 0.34–4.05 %. We also propose a simple method for evaluation of typical element concentrations in plants collected for analyses. Our approach provides a novel screening method for both identification of new hyperaccumulators and for studying a larger number of elements accumulated by plants. This method may find its application in environmental biotechnology.

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Introduction

Plants that are capable of accumulating abnormally high concentrations of trace elements (hyperaccumulators) have been recognized and extensively studied since 1970s. Phytoremediation (Rasico and Navari-Izzo 2011; Ali et al. 2013) and phytomining (Sheoran et al. 2009) are the most important areas of application of these plants. However, the recent studies have suggested a possibility of their use in green nanotechnology (Nath and Banerjee 2013). Approximately 500 taxa have been reported as hyperaccumulators with almost 90 % of known species being endemic to metalliferous soils, such as serpentine soils (Van der Ent et al. 2013). Laboratory experiments based on hydroponic cultures (Tu and Ma 2003; Baldwin and Butcher 2007; Adamidis et al. 2014) and metal-amended soils (Dahmani-Muller et al. 2001) conducted by many researchers in order to find new hyperaccumulators have been criticized as unrealistic (Baker and Whiting 2002; Van der Ent et al. 2013). Comparison of plant responses to metals growing in hydroponics and on natural soil shows that there is a difference in the uptake, accumulation and metabolism of metals (Zabłudowska et al. 2009).

This is the reason why the new studies of hyperaccumulators should encompass the species exhibiting abnormally high element concentrations when growing in natural habitats. In the recent studies of native plant species showing high bioaccumulative properties for potentially toxic elements, only 2–10 elements were determined (Barrutia et al. 2011; Li et al. 2011; Jana et al. 2012; Pratas et al. 2013).

The hyperaccumulators are assumed to show the abundances of chemical species over 2–3 orders of magnitude higher than foliar concentrations of elements in non-hyperaccumulators growing on normal soils or at least one order of magnitude greater than their equivalents growing on metalliferous soils (Van der Ent et al. 2013). This assumption implies an extreme element tolerance (hypertolerance) expressed by hyperaccumulators (Baldwin and Butcher 2007).

Hyperaccumulation of As, Cd, Mn, Ni, Se and Zn has been confirmed, but the uptake status of other elements in plants has to be still established or revised. In our opinion, the most important task for the future hyperaccumulator studies will include identification of new hyperaccumulators of commercially important elements (e.g., rare earth elements) for their possible application in phytomining and new co-accumulators for more effective phytoextraction (Krzciuk and Gałuszka 2014). A method capable of fast and reliable screening of plant species for their hyperaccumulation and co-accumulation is needed to achieve these goals.

A semiquantitative multi-element analysis by inductively coupled plasma mass spectrometry (ICP-MS) is based on measurement of the entire mass spectrum (atomic mass range from ^{7}Li to ^{238}U) and it does not require calibration standards. In the semiquantitative mode, the software uses the table of the response factors for each element and corrects for common interferences reporting approximate concentrations of all elements in the sample. However, to improve the method accuracy and precision and obtain quantitative results the external calibration and the use of internal standards is recommended (Soldevila et al. 1998; Chen et al. 2008). Semiquantitative mode has been widely used for fast screening of unknown samples and to study authenticity and adulteration of food and wine (Shiraishi 1998; Castillo et al. 1999; Almeida and Vasconcelos 2002; Laursen et al. 2009). However, despite its unquestionable potential for screening of samples enriched in trace elements, it has not been applied in prospecting for hyperaccumulators.

The aim of this paper is to present a new two-step screening method for prospecting of trace element accumulating plants, which may find its application in the search for new hyperaccumulators. The proposed methodology can find an application not only to the analysis of plants used in phytoextraction and phytomining, but also to the analysis of edible plants, herbs and stock fodder (Ali et al. 2013; Sheoran et al. 2009; Dutta et al. 2014; Olujimi et al. 2014; Robinson et al. 2005).

Materials and methods

A scientific rationale of the proposed methodology is summarized in Fig. 1.

Sampling

The green parts of 30 plant species (Table 1) were sampled at a height of about 5 cm above ground surface in an abandoned iron- and uranium-ore mining area in the village of Rudki (samples 1–21) and in an residential area (samples 22–30) of the city of Kielce, the Holy Cross Mountains, south-central Poland. Each composite sample weighing about 10 g consisted of about five subsamples taken within an area of about 10 m^2. All samples were placed in polyethylene bags and transported to the laboratory on the day of sampling.

Collection of the aboveground plant samples representing different species growing in the study area is the first step of the proposed methodology. Selection of green plant parts for analysis is in agreement with the definition of hyperaccumulator, which states that hyperaccumulators are plants that accumulate elements in excessive amounts in the aboveground organs (Rasico and Navari-Izzo 2011; Ali et al. 2013; Van der Ent et al. 2013).

Solutions and reagents

During sample digestion, Merck Millipore Poland concentrated nitric acid 65 % Suprapur and hydrogen peroxide 30 % Suprapur were used. All solutions were prepared with high quality deionized water.

Sample preparation

In the laboratory, the samples were carefully cleaned with tap water, rinsed with deionized water and left to dry at an

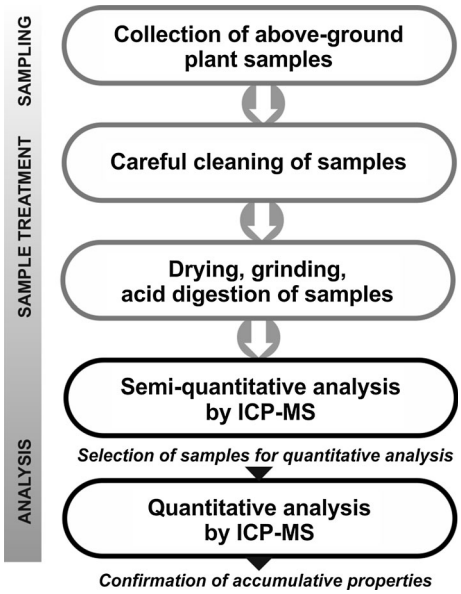

Fig. 1 Schematic view of the proposed methodology that can be used for prospecting of trace element accumulating plants

Table 1 Results of semiquantitative and quantitative determinations of selected elements

Sample number	Species	Analysis mode	Sc	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ag	Cd	Ba	Tl	Pb
			(mg/kg)												
1	*Ranunculus arvensis*	SemiQ.	<0.001	1.00	29	19	<0.001	2.00	6.0	20	<0.001	<0.001	8.0	<0.001	<0.001
2	*Lotus corniculatus*	SemiQ.	<0.001	0.50	19	36	<0.001	1.50	4.0	17	<0.001	<0.001	1.5	<0.001	<0.001
3	*Leucathemum vulgare*	SemiQ.	0.501	1.00	22	26	<0.001	1.00	5.0	16	<0.001	0.501	1.0	<0.001	<0.001
4	*Galium mollugo*	SemiQ.	1.002	0.50	24	32	<0.001	0.50	3.5	18	<0.001	<0.001	15.5	<0.001	<0.001
5	*Trifolium pratense*	SemiQ.	<0.001	0.50	27	50	<0.001	1.00	7.5	19	<0.001	<0.001	4.5	<0.001	<0.001
6	***Tanacetum vulgare***	SemiQ.	0.501	0.50	63	49	<0.001	1.00	10.0	21	<0.001	1.002	148	<0.001	<0.001
		Quantitative	**0.591**	**0.610**	**80**	**58**	**0.049**	**1.190**	**12**	**33**	**0.017**	**0.989**	**162**	**0.039**	**0.362**
7	***Veronica chamaedrys***	SemiQ.	<0.001	1.00	32	105	<0.001	1.00	5.5	20	<0.001	<0.001	251	<0.001	0.501
		Quantitative	**0.107**	**0.817**	**43**	**100**	**0.119**	**1.098**	**6**	**29**	**0.011**	**0.296**	**267**	**0.054**	**0.793**
8	*Mentha arvensis*	SemiQ.	<0.001	1.00	23	62	<0.001	1.00	6.0	31	<0.001	<0.001	2.5	<0.001	<0.001
9	*Hypericum perforatum*	SemiQ.	<0.001	0.50	84	52	<0.001	2.00	8.5	21	<0.001	<0.001	2.5	<0.001	<0.001
10	*Arthemisia vulgaris*	SemiQ.	0.501	1.00	81	76	<0.001	1.50	10.0	15	<0.001	<0.001	6.5	<0.001	<0.001
11	*Trifolium dubium*	SemiQ.	<0.001	1.00	32	96	<0.001	1.50	4.0	15	<0.001	<0.001	5.5	<0.001	<0.001
12	***Plantago media***	SemiQ.	0.501	1.50	10	215	<0.001	1.00	7.5	15	<0.001	<0.001	21.5	<0.001	1.502
		Quantitative	**0.180**	**1.502**	**11**	**186**	**0.107**	**0.931**	**8**	**20**	**0.015**	**0.027**	**27**	**0.051**	**2.18**
13	***Hieracium caespitosum***	SemiQ.	<0.001	1.00	388	57	0.500	13.51	5.5	27	0.5	3.50	0.5	<0.001	<0.001
		Quantitative	**0.074**	**0.840**	**397**	**39**	**0.404**	**12.87**	**5**	**34**	**0.017**	**4.42**	**0.46**	**0.006**	**0.176**
14	***Juncus effusus***	SemiQ	0.5	1.00	1,254	73	1.001	7.51	16.5	50	<0.001	2.502	0.5	<0.001	<0.001
		Quantitative	**0.416**	**0.988**	**1,219**	**49**	**0.786**	**6.542**	**15**	**61**	**0.301**	**2.78**	**0.58**	**0.021**	**0.185**
15	*Lychnis flos-cuculi*	SemiQ.	<0.001	0.50	101	78	<0.001	1.00	4.0	21	<0.001	<0.001	6.5	<0.001	<0.001
16	*Geranium pratense*	SemiQ.	<0.001	0.50	22	67	<0.001	1.50	5.0	13	<0.001	<0.001	14.5	<0.001	<0.001
17	*Alchemilla vulgaris*	SemiQ.	0.501	1.00	85	102	<0.001	1.00	4.5	22	<0.001	0.501	5.5	<0.001	<0.001
18	*Potentilla anserina*	SemiQ.	0.5	1.50	93	141	<0.001	1.50	4.0	17	<0.001	<0.001	17.5	<0.001	<0.001
19	***Equisetum arvense***	SemiQ.	1.00	1.50	29	96	<0.001	1.00	9.0	36	<0.001	0.501	9.0	<0.001	<0.001
		Quantitative	**0.902**	**1.446**	**36**	**72**	**0.079**	**0.788**	**9**	**46**	**0.015**	**0.704**	**13**	**0.013**	**0.127**
20	*Lactuca seriola*	SemiQ.	0.501	0.50	69	66	<0.001	0.50	6.5	25	<0.001	<0.001	1.5	<0.001	<0.001
21	*Euphorbia esula*	SemiQ.	<0.001	1.00	67	85	1.503	1.00	6.5	25	<0.001	<0.001	3.5	<0.001	<0.001
22	*Melilotus officinalis*	SemiQ.	<0.001	0.50	48	93	0.500	1.50	5.5	16	<0.001	<0.001	20.0	<0.001	<0.001
23	***Genista tinctoria***	SemiQ.	<0.001	1.00	127	90	1.001	2.00	7.5	28	<0.001	<0.001	12.0	<0.001	<0.001
		Quantitative	**<0.001**	**0.724**	**106**	**49**	**0.642**	**1.174**	**6.0**	**30**	**0.005**	**0.033**	**14**	**0.003**	**0.189**
24	*Galium verum*	SemiQ.	1.50	1.00	73	78	<0.001	1.50	5.0	30	<0.001	<0.001	39.0	<0.001	<0.001
25	*Agrimonia eupatoria*	SemiQ.	<0.001	1.00	44	100	<0.001	1.50	8.0	19	<0.001	<0.001	10.0	<0.001	<0.001
26	*Symphytum officinale*	SemiQ.	1.50	1.00	33	68	<0.001	1.00	5.0	13	<0.001	<0.001	20.5	<0.001	<0.001
27	*Chamaenerion angustifolium*	SemiQ.	1.00	1.00	15	61	<0.001	1.00	5.5	17	<0.001	<0.001	4.0	<0.001	<0.001

Table 1 continued

Sample number	Species	Analysis mode	Sc	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ag	Cd	Ba	Tl	Pb
			(mg/kg)												
28	***Rorippa amphibia***	SemiQ.	<0.001	0.50	100	81	0.501	0.50	7.0	31	<0.001	<0.001	3.0	0.501	<0.001
		Quantitative	**0.023**	**0.632**	**92**	**53**	**0.267**	**0.42**	**6.0**	**37**	**0.009**	**0.306**	**4.0**	**0.468**	**0.200**
29	***Filipendula ulmaria***	SemiQ.	0.501	1.00	313	86	<0.001	2.51	8.5	39	<0.001	0.501	36.1	<0.001	<0.001
		Quantitative	**0.020**	**0.437**	**259**	**46**	**0.090**	**1.493**	**7.0**	**43**	**0.011**	**0.750**	**38**	**0.005**	**0.153**
30	***Cichorium intybus***	SemiQ.	0.501	2.00	76	118	<0.001	2.50	8.5	22	<0.001	<0.001	8.0	<0.001	<0.001
		Quantitative	**0.098**	**1.488**	**69**	**75**	**0.167**	**1.815**	**7.0**	**25**	**0.007**	**0.127**	**10**	**0.008**	**0.168**

Data in bold represent samples selected for quantitative analyses

ambient temperature in a separate sample storage room with limited access. After drying, the samples were disaggregated using a microfine grinder (Model MF10 basic from IKA-WERKE). The next step of sample preparation for analyses was digestion of 0.5 ± 0.0001 g of each sample with nitric acid (1:1) (8 ml) and hydrogen peroxide (1 ml) in a closed microwave system (Multiwave 3000 from Anton Paar).

The collected samples should be carefully cleaned because as has been shown the elevated levels of elements in the samples may result from surface contamination (passive accumulation), which is not considered hyperaccumulation (Faucon et al. 2007; Van der Ent et al. 2013). The cleaned plants should be dried and ground in order to obtain a homogenous laboratory samples. The next step is acid digestion of samples. Different acids and additional reagents, such as hydrogen peroxide, can be utilized for total digestion of plant samples. Detailed analytical protocols for plant sample treatment prior to the analysis by inductively coupled plasma mass spectrometry can be found in the recent literature (e.g., Mihaylova et al. 2013).

Chemical analyses

We propose that the trace element accumulative properties of plants should first be evaluated with application of semiquantitative analysis mode using the ICP-MS method. The use of this mode enables determination of up to 75 elements on the basis of the entire mass spectrum measurements. This mode substantially shortens the time of analysis and reduces the use of reagents through simplification of analytical procedures. Its advantage over the full quantitative analysis mode employed in the study of accumulation of elements by plants is the possibility of selection of all elements that show a considerable enrichment in the samples analyzed. Although the use of improved semiquantitative mode for plant sample analysis has already been reported as an alternative to quantitative analysis (Zuluaga et al. 2011), it has never been applied to the study of trace element accumulation by plants.

The element determinations were performed using an ICP-MS instrument (model ELAN DRC II, Perkin Elmer). After daily optimization procedure with application of the Elan DRC Setup/Stab/Masscal solution from Perkin Elmer, the samples were analyzed using a semiquantitative analysis mode (TotalQuant) without any external standardization. For the quantitative analysis, a series of calibration standards were prepared from multi-element calibration standards 1 and 2 from Perkin Elmer (element concentrations of 10 mg/l in 5 % HNO_3). The instrumental and data acquisition parameters of the ICP-MS instrument were as follows: sweeps/reading—20, readings/replicate—3, replicates—4, nebulizer gas flow—1.03 L/min, plasma gas

flow—15 L/min, lens voltage—7.50 V, plasma power—1,275 W. Measurements were done in the peak hopping mode and the dwell time was 50–150 μs depending on the analyte. To compensate for the instrument drift during a series of measurements, two internal standards were used: Rh and Ir.

Quality control

For the purpose of quality control, the certified reference material NIST 1573a (Tomato Leaves) was prepared and analyzed with the samples, reagent blanks and digestion blanks. The following percent recovery values of elements from the CRM were found as follows: Cd 83 %; Cr 88 %; Co 89 %; Cu 81 %; Fe 80 %; Mn 97 %; Ni 91 %; Zn 80 %; Ba; 80 %; Ag 103 %. The RSD values were well below 5 % for all analyzed samples, whereas the method uncertainty was below 10 %.

All the chemical analyses of collected samples were performed in the Geochemical Laboratory of the Institute of Chemistry, Jan Kochanowski University in Kielce.

Evaluation of typical element concentrations in plants

Here, we also propose a method that can be used for identification of hyperaccumulators for which the concentration threshold values of the elements have not been established. According to Van der Ent et al. (2013), the minimum concentrations of elements in dry foliage of hyperaccumulators growing in their natural habitats are: 10,000 μg/g for Mn; 3,000 μg/g for Zn; 1,000 μg/g for As, Ni and Pb; 300 μg/g for Co, Cr and Cu; and 100 μg/g for Cd, Se and Tl. The threshold criteria for other elements have not been set, but it has been recommended that hyperaccumulator status can be established if the foliar element concentrations are 50–100 or 100–1,000 times higher than those in plants growing on normal soils (Van der Ent et al. 2013; Cappa and Pilon-Smits 2014). Thus, to confirm the hyperaccumulator status, the typical foliar concentrations should be considered. However, these "normal" concentrations may differ even for the same plant species growing on different soils. Although the elemental composition of a standard reference plant is known (Markert 1992), it seems reasonable to establish typical foliar element concentrations on a local or regional scale. Our method is based on the analysis of at least several plant samples and this gives an opportunity to use chemometrics for establishing the typical foliar concentrations of elements in plants growing in the study area. For this purpose, we propose that the iterative 2σ-technique be used (Matschullat et al. 2000). This technique is frequently employed for calculation of geochemical background. For this purpose, a mean value and standard deviation are calculated for the dataset composed of the results derived from single element determinations in plant samples. All values beyond the mean $\pm 2\sigma$ are omitted, and the new mean $\pm 2\sigma$ range is calculated using the reduced data. This procedure is repeated until all the values of the dataset lie within this range (approaching a normal distribution). The reduced dataset does not contain the outliers, which represent abnormally low and high concentrations of elements. The positive outliers will be of interest in establishing hyperaccumulator status of the plant species examined. We propose the mean value calculated from the reduced dataset as the value representing a typical foliar element concentration in plants growing in the study area.

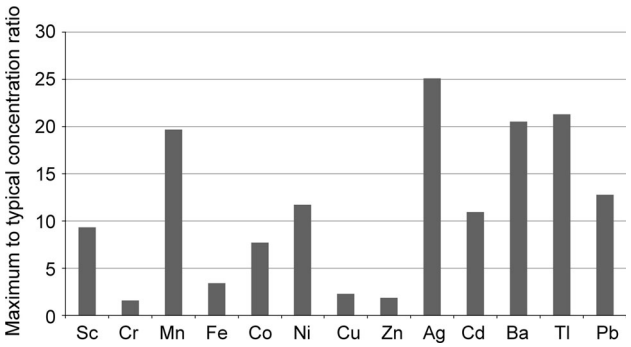

Fig. 2 Maximum to typical element concentration ratios in the examined plant samples

Table 2 Typical element concentrations computed on the basis of the iterative 2σ-technique and the comparison of these results with maximum values obtained from the quantitative analyses

	Sc	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ag	Cd	Ba	Tl	Pb
Typical element concentration[a] (mg/kg)	0.097	0.966	62	55	0.102	1.1	6.7	33	0.012	0.404	13	0.022	0.171
Concentration in a reference plant (mg/kg) (after Markert 1992)	0.02	1.5	200	150	0.2	1.5	10	50	0.2	0.05	40	0.05	1.0
Maximum concentration (mg/kg)	0.902	1.50	1,219	186	0.786	12.9	15	61	0.301	4.42	267	0.468	2.18
Sample no. showing maximum concentration	19	12	14	12	14	13	14	14	14	13	7	28	12

[a] A mean of element concentration computed on the basis of normalized statistical range derived from application of the iterative 2σ-technique

Results and discussion

The results for selected elements, which concentrations determined in the semiquantitative mode are above the detection limits, are presented in Table 1. Major plant constituents are not of interest in hyperaccumulator studies (Van der Ent et al. 2013), and the results for these elements are not discussed here.

Semiquantitative analyses allowed us to select 10 plant species, namely *Tanacetum vulgare*, *Veronica chamaedrys*, *Plantago media*, *Hieracium caespitosum*, *Juncus effusus*, *Equisetum arvense*, *Genista tinctoria*, *Rorippa amphibia*, *Filipendula ulmaria* and *Cichorium intybus* for quantitative analyses. The reason for selection of these samples was their enrichment in one or more trace elements. Many elements were not detected in the semiquantitative mode because of too high detection limits (0.001 mg/kg). However, in the search for hyperaccumulators, much higher concentrations are expected in plant samples and this limitation of the semiquantitative mode should not be considered as a disadvantage. Moreover, the results of semiquantitative and quantitative determinations of elements in our samples were strongly statistically correlated. The Pearson correlation coefficient values were the highest for Ba (0.999), Ni (0.989), Mn (0.997) and Zn (0.917). For many elements (Cr, Mn, Fe, Ni, Cu, Zn and Ba), the semiquantitative mode results are comparable to those obtained by the quantitative mode. Elements that show concentrations <0.001 mg/kg in the semiquantitative mode usually exhibit concentrations >0.001 mg/kg in the quantitative mode. This shows that the semiquantitative mode without external calibration and application of internal standard may be problematic for determination of elements that occur at low concentration levels in the analyzed samples.

The study showed that *J. effusus* accumulated almost 20 times more Mn and 25 times more Ag than the typical plant species from the study area (Fig. 2). The two other species, *V. chamaedrys* and *R. amphibia*, showed about 21 times higher concentrations of Ba and Tl compared to those in the surrounding vegetation.

The results of the quantitative analyses were used to establish the normal foliar concentrations of elements in vegetation of the study area with application of the iterative 2σ-technique (Table 2). The typical foliar element concentrations, except for Sc and Cd, were lower than the concentrations of elements reported for a reference plant (Markert 1992). This observation indicates that the use of reference plant data for evaluation of element accumulative properties of plants is unsuitable, and it may lead to underestimation of the results.

None of the collected plants met the hyperaccumulator criteria. The highest enrichment in the determined elements was found in sample 14 (*J. effusus*) (Fig. 3). This plant species is known for its extremely high biomass production rates (Wetzel and Howe 1999). This feature accompanied with accumulation of Mn may favor the use of *J. effusus* in phytoextraction.

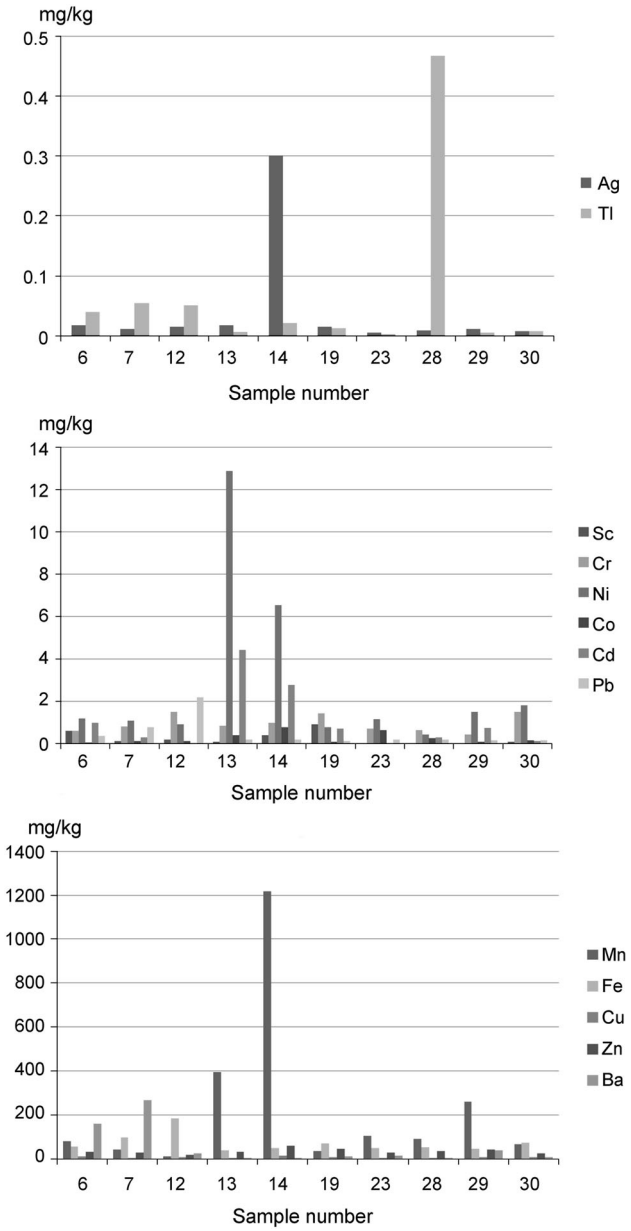

Fig. 3 Concentrations of elements in plant samples obtained in quantitative analyses

Conclusion

The results of semiquantitative analysis allow us to select both the plant samples and individual elements for a quantitative determination. This approach may greatly facilitate the identification of hyperaccumulators and co-accumulators of trace elements. Although the detection

limits of semiquantitative analysis are higher than those of quantitative analysis, this disadvantage does not discredit the use of our method to the study of hyperaccumulators because the element concentrations in these plants are well above the detection limits.

Our novel approach to identification of trace element accumulating plants using a semiquantitative mode of analysis prior to the quantitative element determinations provides the possibility for identification of plants suitable for phytoextraction and phytomining. The advantages of our methodology compared with the methods that are currently applied in prospecting for new hyperaccumulators are the following: (1) broadening the number of determined elements, (2) studying the plants that grow in their natural habitats and (3) establishing reliable typical concentrations of elements in aboveground organs of the plants in a given study area.

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