

QUANTITATIVE RELATIONS BETWEEN THE CONTENT OF SELECTED TRACE ELEMENTS IN SOIL EXTRACTED WITH 0.03 M CH₃COOH OR 1 M HCl AND ITS TOTAL CONCENTRATION IN LETTUCE AND SPINACH

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Abstract. Numerous analytical methods have been developed for determination of micro-nutrients, heavy metals and trace elements in soil. However, rapid and easy-to-perform methods are still needed for chemical composition analysis of soil that would be based on simultaneous extraction of multiple elements. Furthermore, it would be beneficial if element concentration in soil using these methods were correlated with its concentration in plants. The aim of the study was to determine the interdependency between soil concentration of: Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, Ti, V and Zn extracted using 0.03 M CH₃COOH or 1 M HCl and its content in spinach leaves and lettuce heads. In reference to Al, B, Ba, Cd, Mn, Ni and Zn level in spinach as well as Al, B, Ba, Cd, Cr, Fe, Li and Ti accumulation in lettuce, higher values of correlation coefficients were calculated for soil and plant content of these elements after extraction with 0.03 M CH₃COOH than 1 M HCl. In the case of: Cr, Cu, Fe, Li and Sr in spinach as well as Ni and Pb in lettuce, higher values of this parameter were found for 1 M HCl soil extraction when compared with the other tested method. No significant relation was found between Pb and Ti accumulation in spinach as well as Cu, Mn, Sr or Zn content in lettuce and its level in soil irrespective of the extraction method (0.03 M CH₃COOH or 1 M HCl).

Key words: 0.03 M acetic acid, 1 M hydrochloride acid, Rinkis method, trace elements

INTRODUCTION

In diagnostics of plant fertilization needs these methods are preferred that enable determining multiple available forms of mineral nutrients in one extraction medium [Nowosielski 1974, Komosa 2000]. There is a tendency to use solutions of weaker ex-

traction power but strongly correlating with the amount of mineral nutrients uptaken by plants [Komosa and Stafecka 2002].

In Poland, for the purposes of chemical analysis of soils and substrates for horticultural production (excluding pomology), 0.03 M CH_3COOH extraction is commonly used for macro element and boron determination (the universal method) while Lindsay method- for the estimation of other micronutrients [Nowosielski 1974]. In the latter method, extraction medium consists of: EDTAH_4 , NH_3 , $\text{C}_3\text{H}_8\text{O}_7\text{H}_2\text{O}$ and $(\text{CH}_3\text{COO})_2\text{Ca}\cdot 2\text{H}_2\text{O}$. Soil extraction using 1 M HCl – Rinkis method [Gorlach et al. 1999] – is applied for some microelement determination in agricultural soils. This method, in comparison to Lindsay method, is much more convenient particularly in respect of medium preparation as well as soil extract storage. Tyksiński [1985] showed differentiated extraction ability of Lindsay solution in reference to: Cu, Fe, Mn, Mo and Zn which varied from 32% for Mo to 96% for Mn.

Other soil extraction methods basing on a single solution are also applied. In the Netherlands, soil preparation with 0.01 M CaCl_2 is used [Houba et al. 1997] as well as peat substrate extraction by distillate water. In Germany soil extraction with CaCl_2 and DTPA mixture is commonly applied [Nowak and Strojny 2004, Strojny and Nowak 2004]. A major disadvantage of using CaCl_2 solutions is though the impossibility of calcium and chloride determination in analyzed soils and substrates. Still, it was shown that soil preparation with 0,01 M CaCl_2 is suitable for assaying in a single extractor easily soluble forms of Cu, Cd, Mn and Zn (as well as, to a lesser extent, Fe) in soil of differentiated physicochemical properties [Sady et al. 1998]. In further research, however, no relation was found between accumulation of: micronutrients, heavy metals and trace elements in carrot storage roots (except Mn and Sr [Smoleń and Sady 2009]) and its level in soil determined after extraction with 0.01 M CaCl_2 [Smoleń and Sady 2006, 2007a, 2007b, 2008, 2009].

The aim of the present study was to evaluate the relationship between soil content of: Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, Ti, V and Zn extracted using 0.03 M CH_3COOH or 1 M HCl and its level in spinach leaves and lettuce heads.

MATERIAL AND METHODS

In 2008–2009 studies were conducted on spinach leaves and lettuce heads as well as soil samples after cultivation of these species. Lettuce ‘Melodion F_1 ’ was cultivated in field experiments on soil classified as fen soil (soil texture class – silty clay: sand 14%, silt 45%, clay 41%). Spinach was grown in pot experiments in containers sized $60 \times 40 \times 20$ cm on the same type of soil. Research was carried out in Experimental Station of Agricultural University in Kraków. Results of chemical analysis of soil before spinach and lettuce cultivation were presented in table 1.

In both years of the study lettuce was cultivated from seedling. Seed sowing was performed in the beginning of March while planting (with spacing of 30×30 cm) – in the middle of April. Lettuce harvest combined with taking soil samples was completed in the beginning of June. In 2008–2009, analysis of chemical composition was carried out on 64 samples of lettuce heads as well as 64 samples of soil after lettuce cultivation taken from 0–30 cm soil layer.

Table 1. Chemical properties of soil before lettuce cultivation in field experiments (in 0–30 cm soil layer) and spinach cultivation in pot experiments in 2008–2009

Tabela 1. Chemiczne właściwości gleby przed uprawą sałaty w doświadczeniach polowych (w warstwie gleby 0–30 cm) oraz szpinaku w doświadczeniach wazonowych w latach 2008–2009

Element Pierwiastek	Before cultivation – Przed uprawą			Before cultivation – Przed uprawą		
	spinach – szpinak	lettuce – sałata	spinach – szpinak	lettuce – sałata	spinach – szpinak	lettuce – sałata
	extraction 0.03 M CH ₃ COOH, mg·dm ⁻³ soil ekstrakcja 0.03 M CH ₃ COOH, mg·dm ⁻³ gleby	extraction 0.03 M CH ₃ COOH, mg·dm ⁻³ soil ekstrakcja 0.03 M CH ₃ COOH, mg·dm ⁻³ gleby	extraction 1 M HCl, mg·kg ⁻¹ soil ekstrakcja 1 M HCl, mg·kg ⁻¹ gleby	extraction 1 M HCl, mg·kg ⁻¹ soil ekstrakcja 1 M HCl, mg·kg ⁻¹ gleby	extraction 1 M HCl, mg·kg ⁻¹ soil ekstrakcja 1 M HCl, mg·kg ⁻¹ gleby	extraction 1 M HCl, mg·kg ⁻¹ soil ekstrakcja 1 M HCl, mg·kg ⁻¹ gleby
Al	3.0–3.6	1.88–2.25	0.7–3.4	0.44–2.13	1358.0–1176.8	1338.4–1001.5
B	1.1–1.1	0.69–0.69	1.1–1.2	0.69–0.75	n.d./b.d.–1.1	n.d./b.d.–1.7
Ba	3.8–3.2	2.38–2.00	3.3–3.1	2.06–1.94	47.6–50.8	54.4–46.6
Cd	0.02–0.03	0.01–0.02	0.02–0.04	0.01–0.03	1.0–0.9	1.0–0.9
Co	0.01–<0.003	0.01–<0.002	0.003–<0.003	<0.002–<0.002	1.7–1.0	1.8–1.2
Cr	0.01–0.01	0.01–0.01	0.004–0.02	0.003–0.01	1.7–1.0	1.7–1.1
Cu	<0.002–0.07	<0.001–0.04	<0.002–0.02	<0.001–0.01	4.3–4.8	5.2–6.0
Fe	0.3–0.5	0.19–0.31	0.1–0.9	0.06–0.56	2238.4–1291.5	2787.2–1617.9
Li	0.01–0.03	0.01–0.02	0.02–0.03	0.01–0.02	0.8–0.4	0.7–0.3
Mn	1.1–1.1	0.69–0.69	1.2–2.01	0.75–1.26	281.1–163.2	328.5–190.9
Mo	<0.01–<0.01	<0.006–0.01	<0.01–<0.01	<0.006–<0.006	<0.01–<0.01	<0.01–<0.01
Ni	0.1–0.1	0.06–0.06	0.05–0.11	0.03–0.07	2.9–2.8	3.1–2.5
Pb	0.02–0.03	0.01–0.02	<0.01–<0.01	0.01–0.01	25.8–20.9	28.8–22.5
Sr	7.6–5.1	4.75–3.19	7.2–4.1	4.50–2.56	13.9–15.3	13.8–13.5
Ti	<0.01–<0.01	<0.006–0.01	<0.01–0.02	<0.006–0.01	6.7–3.8	7.1–4.2
V	<0.001–<0.001	<0.001–<0.001	<0.001–<0.001	<0.001–<0.001	7.3–5.3	8.1–6.7
Zn	2.1–2.1	1.31–1.31	4.3–2.7	2.69–1.69	50.7–45.3	64.8–46.2
Other parameters – Pozostałe parametry						
pH _{H2O}	6.41–7.09			6.41–6.73		
EC, mS·cm ⁻¹	0.07–0.24			0.07–0.12		
Organic matter, % Materia organiczna, %	2.43–3.39			3.41–3.76		

In 2008, a pot cultivation of spinach was carried out in the open field under a shade providing fabric. Seeds were sown in the beginning of April while harvest with taking soil samples was performed in the third decade of May. Totally, 24 samples of spinach leaves as well as 24 soil samples after spinach cultivation were collected for chemical analysis. In 2009, pot experiment on spinach was carried out in a foil tunnel. Seed sowing was performed in the second decade of March while spinach harvest – at the end of April. Analysis of chemical composition was carried out on 50 samples of spinach leaves as well as 50 soil samples after spinach cultivation. In both years of the study, mean weight of leaf sample was approximately 0.6 kg.

Before spinach sowing and lettuce planting NPK fertilization was performed on the basis of chemical analysis of soil to the level recommended for cultivated species [Sady 2006].

In plant and soil samples (both prior to and after spinach and lettuce cultivation) content of: Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, Ti, V and Zn was determined by ICP-OES method using high-resolution spectrometer (Prodigy Teledyne Leeman Labs). The ICP-OES instrument was calibrated using Merck's ICP multi-element standard no. VI and no. XVI. The soil level of tested elements was determined using two extraction methods. 0,03 M CH_3COOH procedure was applied for soil samples at its natural humidity – the universal method [Nowosielski 1974] while extraction with 1 M HCl was carried out on air-dried, ground and 1 mm – sieved soil samples – Rinkis method [Gorlach et al. 1999]. Concentration of tested elements in plant samples was assayed after mineralization in 65% super pure HNO_3 (Merck no. 100443.2500) in a CEM MARS-5 Xpress microwave oven [Paślawski and Migaszewski 2006].

Total number of analyzed samples allowed to obtain normal distribution for the content of major number of tested elements both in soil and plant material – detailed data not presented.

Obtained results were statistically verified by Statistica 8.0 PL programme for significance level $P < 0.05$. Correlation coefficients were calculated for the relation between soil concentration of elements (after extraction using 0.03 M CH_3COOH or 1 M HCl – x variable) and its content in spinach leaves and lettuce heads – y variable (tab. 2 and 3).

RESULTS AND DISCUSSION

When determining the relation between soil and plant content of mineral element, the following factors should be taken into consideration: physicochemical properties of soil, type of soil analysis procedure as well as plant species. Roots usually accumulate higher amounts of mineral elements than above-ground parts (i.e. shoots and leaves) which in turn contain higher level of minerals than flowers, fruits and seeds [Ramos et al. 2002, Sękara et al. 2005, Bosiacki 2008, 2009]. Among vegetable crops, root and leafy vegetables tend to accumulate considerable amount of heavy metals, especially cadmium [Starck 1992, Sękara et al. 2005].

The level of heavy metal and trace element uptake by plants is basically dependent on numerous physicochemical properties of soil, including content of these elements in

soil [Gerritse et al. 1983, Starck 1992, Şekara et al. 2005]. Concentration of these compounds in soil solution is in turn affected by soil pH as well as chemical properties of particular element. [Tyler and Olsson 2001].

Studies conducted by Davies [1992] revealed that the level of Cd, Pb and Zn in radish roots and leaves was significantly correlated with both soil content of its easily soluble forms (determined in 0.05 M EDTA and 1 M NH_4NO_3) as well as total soil content assayed in concentrated HNO_3 . In research carried out by McLaughlin et al. [1997] no interrelationship was found between cadmium content in soil (extracted for 7 days using 0.05 M EDTA) and its accumulation in potato tubers. On the other hand, Cd accumulation and its total uptake by oat, ryegrass, carrot and spinach plants were significantly correlated with the soil cadmium extracted by DTPA and NH_4NO_3 [He and Singh, 1993]. Gerritse and co-workers [1983] revealed a significant correlation between concentration of: Cd, Cu and Zn in soil solution as well as its easily soluble forms in soil (extracted using 0.005 N and in 0.05 N $\text{CaCl}_2 + \text{NaCl} + \text{KCl}$ in the ratio 3:1:1) and its accumulation in spinach, lettuce and potato. In that study no significant relationship between plant uptake and soil solution concentration or any other soil parameter could be found for Pb analysis. In research conducted by Smoleń [2009], 0.03 M solution of CH_3COOH was suggested a possible of extracting solution for soil level determination of Al, As, Ba, Cd, Cu, Fe, Li, Mn, Ni, Pb, Sr and Zn .

In the present work a differentiated interrelationship was revealed between soil content of tested element (extracted using 0.03 M CH_3COOH and 1 M HCl) and its concentration in spinach and lettuce (tab. 2 and 3). This observation indicates a species-dependency in uptake and accumulation of tested elements in analyzed plant parts. Significant values of correlation coefficients between element content in soil extracted using both methods and its accumulation in plants were calculated in reference to: Al, B, Ba, Cd, Cr, Cu, Fe, Li and Zn in spinach leaves as well as Al, B, Ba, Cd, Cr, Fe, Li and Ni in lettuce heads. These relations, in reference to mentioned elements, were positive or negative for particular vegetable species depending on applied soil extraction method (0.03 M CH_3COOH or 1 M HCl).

A better match (i.e. higher values of correlation coefficients irrespective of its sign) between plant and soil element concentration after 0.03 M CH_3COOH extraction (in comparison to 1 M HCl) was found for Al, B, Ba, Cd, Mn, Ni and Zn in spinach as well as Al, B, Ba, Cd, Cr, Fe, Li and Ti in lettuce (tab. 2 and 3). Observed relation could have resulted from greater extraction efficiency exhibited by 1 M HCl. It was previously shown that application of strong solution extractants usually negatively affects the correlation between soil and plant concentration of most mineral elements [Westerman 1990].

Determination of tested elements in 1 M HCl soil extracts (when compared to 0.03 M CH_3COOH) contributed to higher values of correlation coefficients in reference to spinach content of: Cr, Cu, Fe, Li and Sr as well as lettuce accumulation of Ni and Pb (tab. 2 and 3).

Quantitative chemical analysis in 0.03 M CH_3COOH revealed that the level of: Co, Mo and V in soil after both spinach and lettuce cultivation was below the limits of its detection using ICP-OES spectrometer (tab. 2 and 3). However, after soil extraction with 1 M HCl, a significant interrelationship between soil and plant concentration was found in reference to: Co, V in both species as well as Mo in spinach.

Table 2. Interrelationships between element contents in soil and spinach cultivated in pot experiments (mean from 2008–2009)
 Tabela 2. Zależności pomiędzy zawartością pierwiastków w glebie i w szpinaku uprawianym w doświadczeniach wazonowych (średnie z lat 2008–2009)

Element Pierwiastek	Soil extraction method – mean content of element in soil			Element content in spinach			Soil extraction method – mean content of element in soil			Element content in spinach		
	Metoda ekstrakcji gleby – średnia zawartość pierwiastka w glebie			Zawartość pierwiastka w szpinaku			Metoda ekstrakcji gleby – średnia zawartość pierwiastka w glebie			Zawartość pierwiastka w szpinaku		
	A (mg·dm ⁻³)	A ¹ (mg·kg ⁻¹)	B (mg·kg ⁻¹)	(x)	(n = 74)	A (mg·dm ⁻³)	A ¹ (mg·kg ⁻¹)	B (mg·kg ⁻¹)	(x)	(n = 74)	A (mg·dm ⁻³)	A ¹ (mg·kg ⁻¹)
Al	2.68	1.68	1 216.66		257.13	0.91	0.57	207.07		42.79		
(r)	(-0.77*)	(-0.77*)	(0.75*)		(r)	(-0.81*)	(-0.81*)	(-0.21)		(r)	(-0.81*)	(-0.21)
B	0.76	0.48	1.05		18.99	n.d. / b.d.	n.d. / b.d.	0.19		0.20		
(r)	(0.78*)	(0.78*)	(0.73*)		(r)	(-)	(-)	(-0.69*)				
Ba	2.27	1.42	50.44		6.10	0.09	0.06	2.83		1.25		
(r)	(-0.90*)	(-0.90*)	(0.60*)		(r)	(-0.70*)	(-0.70*)	(0.02)		(r)	(-0.70*)	(0.02)
Cd	0.03	0.02	0.89		2.02	0.05	0.03	20.84		0.24		
(r)	(-0.90*)	(-0.90*)	(0.86*)		(r)	(-0.06)	(-0.06)	(0.05)		(r)	(-0.06)	(0.05)
Co	n.d. / b.d.	n.d. / b.d.	1.33		0.10	4.13	2.58	17.39		40.86		
(r)	(-)	(-)	(0.39*)		(r)	(-0.12)	(-0.12)	(0.26*)				
Cr	0.01	0.006	1.19		1.43	0.02	0.01	3.68		14.60		
(r)	(-0.76*)	(-0.75*)	(0.82*)		(r)	(0.03)	(0.03)	(0.03)		(r)	(0.03)	(0.03)
Cu	0.07	0.04	4.71		7.90	n.d. / b.d.	n.d. / b.d.	6.00		0.44		
(r)	(-0.56*)	(-0.56*)	(0.63*)		(r)	(-)	(-)	(0.24*)		(r)	(-)	(0.24*)
Fe	0.63	0.39	1 390.82		270.19	1.72	1.08	43.34		123.00		
(r)	(-0.37*)	(-0.37*)	(0.60*)		(r)	(-0.81*)	(-0.81*)	(0.58*)				
Li	0.02	0.01	0.53		0.56							
(r)	(-0.72*)	(-0.72*)	(0.77*)									

¹Values recalculated from (mg·dm³) to (mg·kg⁻¹) – Wartości przeliczone z (mg·dm³) na (mg·kg⁻¹)
²n = 50 for Mo, Pb, Ti and V in soil and plant samples (samples only from 2009) – n = 50 dla Mo, Pb, Ti i V w próbach gleby i rośliny (próbki tylko z 2009 roku).
 A – 0.03 M CH₃COOH, B – 1 M HCl. * – Correlation coefficient significant for P ≤ 0.05 – Współczynnik korelacji istotny dla P ≤ 0.05.
 n.d. – no data available – soil content of element after extraction using 0.03 M CH₃COOH below the limits of detection by ICP-OES spectrometer
 b.d. – brak danych – zawartość pierwiastka w glebie po ekstrakcji 0,03 M CH₃COOH poniżej limitu detekcji spektrometru ICP-OES.

Table 3. Interrelationship between element contents in soil and lettuce cultivated in field experiments (mean from 2008–2009)
 Tabela 3. Zależność pomiędzy zawartością pierwiastków w glebie i w sałacie uprawianej w doświadczeniach polowych (średnie z lat 2008–2009)

Element Pierwiastek	Soil extraction method – mean content of element in soil				Soil extraction method – mean content of element in soil				Element content in lettuce Zawartość pierwiastka w sałacie (n = 64)	Element content in lettuce Zawartość pierwiastka w sałacie (n = 64)
	Metoda ekstrakcji gleby – średnia zawartość pierwiastka w glebie (n = 64)		Metoda ekstrakcji gleby – średnia zawartość pierwiastka w glebie (n = 64)		Metoda ekstrakcji gleby – średnia zawartość pierwiastka w glebie (n = 64)		Metoda ekstrakcji gleby – średnia zawartość pierwiastka w glebie (n = 64)			
	A (mg·dm ⁻³)	B (mg·kg ⁻¹)	A ¹ (mg·kg ⁻¹)	B (mg·kg ⁻¹)	A (mg·dm ⁻³)	A ¹ (mg·kg ⁻¹)	B (mg·kg ⁻¹)	B (mg·kg ⁻¹)		
Al	2.21	1 323.51	1.38	1 323.51	Mn	1.40	0.88	300.95	44.97	
(r)	(-0.94*)	(0.55*)	(-0.94*)	(0.55*)	(r)	(-0.13)	(-0.13)	(-0.07)		
B	0.85	1.52	0.53	1.52	Mo	n.d. / b.d.	n.d. / b.d.	n.d. / b.d.	0.93	
(r)	(-0.41*)	(0.37*)	(-0.41*)	(0.37*)	(r)	(-)	(-)	(-)		
Ba	1.83	51.80	1.44	51.80	Ni	0.07	0.04	2.63	1.09	
(r)	(-0.93*)	(0.91*)	(-0.93*)	(0.91*)	(r)	(0.28*)	(0.28*)	(-0.36*)		
Cd	0.02	1.01	0.015	1.01	Pb ²	0.06	0.04	27.33	0.52	
(r)	(0.78*)	(-0.69*)	(0.77*)	(-0.69*)	(r)	(0.001)	(0.006)	0.31*		
Co	n.d. / b.d.	1.84	n.d. / b.d.	1.84	Sr	2.81	1.76	13.65	25.21	
(r)	(-)	(-0.63*)	(-)	(-0.63*)	(r)	(0.22)	(0.22)	(0.12)		
Cr	0.01	1.54	0.008	1.54	Ti	0.89	0.56	8.07	14.66	
(r)	(-0.71*)	(0.58*)	(-0.71*)	(0.58*)	(r)	(0.57*)	(0.57*)	(0.24)		
Cu ²	0.10	6.32	0.06	6.32	V	n.d. / b.d.	n.d. / b.d.	8.47	0.37	
(r)	(-0.11)	(0.25)	(-0.12)	(0.25)	(r)	(-)	(-)	(-0.43*)		
Fe	1.47	2 491.14	0.92	2 491.14	Zn	1.73	1.08	56.32	69.32	
(r)	(-0.81*)	(-0.61*)	(-0.81*)	(-0.61*)	(r)	(0.22)	(0.22)	(-0.09)		
Li	0.02	0.66	0.016	0.66						
(r)	(-0.70*)	(0.33*)	(-0.70*)	(0.33*)						

¹Values recalculated from (mg·dm⁻³) to (mg·kg⁻¹) – Wartości przeliczone z (mg·dm⁻³) na (mg·kg⁻¹)

²For Cu and Pb n = 36 (correlation coefficient calculated only for samples from 2009) – Dla Cu i Pb n = 36 (współczynnik korelacji obliczony tylko dla prób z 2009 r.).

A – 0.03 M CH₃COOH, B – 1 M HCl. * – Correlation coefficient significant for P ≤ 0,05 – Współczynnik korelacji istotny dla P ≤ 0,05.

n.d. – no data available – soil content of element after extraction using 0.03 M CH₃COOH below the limits of detection by ICP-OES spectrometer

b.d. – brak danych – zawartość pierwiastka w glebie po ekstrakcji 0,03 M CH₃COOH poniżej limitu detekcji spektrometru ICP-OES.

In the case of spinach level of Pb and Ti as well as Cu Mn, Sr and Zn contents in lettuce no significant relation was found between its content in plants and soil determined using both extricating solution (tab. 2 and 3).

In study conducted by Smoleń et al. [2010] soil depth-range from which samples were collected had a significant effect on values of correlation coefficients for soil and carrot root content of: Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, Ti, V and Zn extracted using 0.03 M CH₃COOH or 1 M HCl. Analysis carried out in 1 M HCl solution revealed a significant interrelationship between soil and plant content of: Mn and Fe (for 30–60 cm and 60–90 cm soil layers), Co and Pb (for 30–60 cm layer) as well as Mo (for 0–30 cm, 30–60 cm and 60–90 cm layers). These authors also showed that soil level of: Al, B, Ba, Cd, Cu, Sr i Zn (for 0–30 cm, 30–60 cm and 60–90 cm layers) as well as Cr, Li and Ni (for 30–60 and 60–90 cm layers) assayed in 0.03 M CH₃COOH was relatively strongly correlated with its content in carrot when compared to determination using 1 M HCl.

To sum up, results obtained in the present and previous works [Smoleń et al. 2010], allow to state that soil extraction with 0.03 M CH₃COOH can be an adequate procedure for determination of soil content not only in the case of macro elements and chlorides, boron but also Al, Ba, Cd, Cr, Fe, Li, Mn, Ni, Sr, Ti and Zn. Evaluation of usefulness of this procedure for analyzing mentioned elements in soil is though dependent on soil layer from which samples are taken [Smoleń et al. 2010] as well as the level of mineral uptake by particular plants species. It is thus proposed that further studies should be carried out on soils with differentiated physicochemical properties along with complex assessment of plant nutrition with macro- and microelements as well as trace element accumulation in cultivated plants

CONCLUSIONS

For spinach content of: Al, B, Ba, Cd, Cr, Cu, Fe, Li and Zn as well as lettuce level of: Al, B, Ba, Cd, Cr, Fe, Li and Ni a significant relation was found between soil and plant content of these elements after soil extraction with 0.03 M CH₃COOH and 1 M HCl.

Significantly higher values of correlation coefficients for plant and soil content of elements determined using 0.03 M CH₃COOH (in comparison to 1 M HCl extraction) were found in reference to: Al, B, Ba, Cd, Mn, Ni and Zn in spinach leaves as well as Al, B, Ba, Cd, Cr, Fe, Li and Ti in lettuce.

Significantly higher values of correlation coefficients for soil extraction with 1 M HCl (when compared to 0.03 M CH₃COOH extraction) and its content in plants were found in respect of: Cr, Cu, Fe, Li and Sr in spinach as well as Ni and Pb in lettuce.

No significant relation was found for Pb and Ti content in spinach as well as Cu, Mn, Sr and Zn accumulation in lettuce and its level in soil assayed in both 0.03 M CH₃COOH and 1 M HCl extracts.

REFERENCES

- Bosiacki M., 2008. Accumulation of cadmium in selected species of ornamental plants. Acta Sci. Pol. Hortorum Cultus 7 (2), 21–31.
- Bosiacki M., 2009. Phytoextraction of cadmium and lead by selected cultivars of *Tagetes erecta* L. Part II. Contents of Cd and Pb in plants. Acta Sci. Pol. Hortorum Cultus 8 (2), 15–26.
- Davies B.E., 1992. Inter-relationships between soil properties and the uptake of cadmium, copper, lead and zinc from contaminated soils by radish (*Raphanus sativus* L.). Water Air and Soil Poll. 63, 331–342.
- Gerritse R.G., Van Driel W., Smilde K.W., Van Luit B., 1983. Uptake of heavy metals by crops in relation to their concentration in the soil solution. Plant and Soil 75, 393–404.
- Gorlach E., Curyło T., Gambuś F., Grzywnowicz I., Jasiewicz C., Kopeć M., Mazur B., Olkuśnik S., Rogóż A., Wiśniowska-Kielian B., 1999. Przewodnik do ćwiczeń z chemii rolnej. Wyd. AR w Krakowie.
- He Q.B., Singh B.R., 1993. Crop uptake of cadmium from phosphorus fertilizers: II. Relationship with extractable soil cadmium. Water Air Soil Poll. 74, 267–280.
- Houba V.J.G., Novozamsky I., Temminghoff E., 1997. Soil analysis procedures. Extraction with 0.01 M CaCl₂ (Soil and Plant Analysis, Part 5A). Wageningen Agricultural University, The Netherlands.
- Komosa A., 2000. Nowoczesne diagnozowanie potrzeb nawozowych roślin sadowniczych. Mat. konf. VIII Ogólnopolskiej Konferencji Naukowej pt. „Efektywność Stosowania nawozów w uprawach ogrodnictwa. Zmiany ilościowe i jakościowe w warunkach stresu. Warszawa 20–21 czerwca 2000, 11–16.
- Komosa A., Stafecka A., 2002. Zawartości wskaźnikowe składników pokarmowych dla gleb sadowniczych analizowanych metodą uniwersalną. Roczn. AR w Poznaniu 341, Ogrodnictwo 35, 105–116.
- McLaughlin M.J., Maier N.A., Rayment G.E., Sparrow L.A., Berg G., McKay A., Milham P., Merry R.H., Smart M.K., 1997. Cadmium in Australian potato tubers and soils. J. Environ. Qual. 26, 1644–1649.
- Nowak J.S., Strojny Z., 2004. Metody analizy chemicznej podłoża ogrodnictwa stosowane w Holandii i w Niemczech w celach diagnostycznych. Roczn. AR w Poznaniu 356, Ogrodnictwo 37, 255–259.
- Nowosielski O., 1974. Metody oznaczania potrzeb nawożenia. Wyd. II. PWRiL, Warszawa.
- Paślawski P., Migaszewski Z.M., 2006. The quality of element determinations in plant materials by instrumental methods. Polish J. Environ. Stud. 15(2a) Part I, 154–164.
- Ramos I., Esteban E., Lucena J.J., Garate A., 2002. Cadmium uptake and subcellular distribution in plants of *Lactuca* sp. Cd-Mn interaction. Plant Sci. 162, 761–767.
- Sady W., 2006. Nawożenie warzyw polowych. Plantpress, Kraków.
- Sady W., Rożek S., Domagała I., Kołodziej M., 1998. Porównanie metod ekstrakcji Cu, Zn, Mn, Fe, i Cd z gleb o zróżnicowanych właściwościach fizykochemicznych. Zesz. Nauk. AR w Krakowie 333 (57), 833–836.
- Sękara A., Poniedziałek M., Ciura J., Jędrszczyk E., 2005. Cadmium and lead accumulation and distribution in the organs of nine crops: implications of phytoremediation. Polish J. of Environ. Stud. 14 (4), 509–516.
- Smoleń S., 2009. Wpływ nawożenia jodem i azotem na skład mineralny marchwi. Ochr. Środ. i Zas. Nat. In print.
- Smoleń S., Sady W., 2006. The content of Cd, Cu and Zn in carrot storage roots as related to differentiated nitrogen fertilization and foliar nutrition. Polish J. Environ. Stud. 15 (2A, Part II), 503–509.

- Smoleń S., Sady W., 2007a. The effect of nitrogen fertilizer form and foliar application on Cd, Cu and Zn concentrations in carrot. *Folia Hort.* 19 (1), 87–96.
- Smoleń S., Sady W., 2007b. Wpływ nawozu azotowego z inhibitorem nityfikacji oraz dokarmiania dolistnego na zawartość suchej masy, Cd, Cu i Zn w marchwi. *Ochr. Środ. i Zas. Nat.* 32: 81–86.
- Smoleń S., Sady W., 2008. The effect of foliar nutrition with nitrogen, molybdenum, sucrose and benzyladenine on the contents of dry weight, Cd, Cu and Zn in carrot. *Veget. Crops Res. Bull.* 68, 135–144.
- Smoleń S., Sady W., 2009. The effect of nitrogen fertilizer form and foliar application on concentrations of twenty five elements in carrot. *Folia Hort.* 21 (1), 3–16.
- Smoleń S., Sady W., Ledwożyw I. 2010. Usefulness of soil extraction with 0.03 M CH₃COOH and 1 M HCl for estimation of selected trace elements accumulation in carrot. *Acta Sci. Pol. Hortorum Cultus* 9(4), 3–12.
- Starck J.R., 1992. Wpływ nawożenia na gromadzenie metali ciężkich w roślinach. *Mat. Konf. Nauk. pt. „Stan i przyczyny skażenia żywności metalami”*, Toruń 14–15 marca 1988, 19–23.
- Strojny Z., Nowak J.S., 2004. Zasady metodyki analizy chemicznej podłoża ogrodniczych przyjętej przez Unię Europejską. *Rocz. AR w Poznaniu* 356, *Ogrodnictwo* 37, 279–286.
- Tyksiński W., 1985. Reakcja sałaty szklarniowej uprawianej w torfie na zróżnicowane nawożenie mikroelementami. Cz. II. Zmiany zawartości mikroelementów w podłożu. *Prace Komisji Nauk Roln. i Leśnych.* LIX, 243–251.
- Tyler G., Olsson T., 2001 Concentrations of 60 elements in the soil solution as related to the soil acidity. *Europ. J. Soil Sci.* 52, 151–165.
- Westerman R.L., 1990. *Soil testing and plant analysis.* 3rd edition. Soil. Sci. Soc. Amer., Madison, Wi.

RELACJE IŁOŚCIOWE MIĘDZY ZAWARTOŚCIĄ WYBRANYCH PIERWIĄSTKÓW ŚLADOWYCH W GLEBIE EKSTRAHOWANYCH 0,03 M CH₃COOH I 1 M HCL A ZAWARTOŚCIĄ ICH FORM OGÓLNYCH W SAŁACIE I SZPINAKU

Streszczenie. Opracowano wiele metod oznaczania zawartości mikroskładników, metali ciężkich oraz pierwiastków śladowych w glebie. Jednakże nadal istnieje potrzeba poszukiwania szybkich i łatwych do wykonania metod analizy składu chemicznego gleby, które byłyby oparte na wspólnej ekstrakcji wielu składników. Najlepiej, by zawartość składników oznaczona w glebach za pomocą tych metod była skorelowana z ich zawartością w roślinach. Celem badań było określenie zależności pomiędzy zawartością w glebie Al, B, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sr, Ti, V i Zn ekstrahowanych za pomocą 0,03 M CH₃COOH (metoda uniwersalna) i 1 M HCl (test Rinkisa), a ich zawartością w liściach szpinaku i w główkach sałaty. W odniesieniu do zawartości: Al, B, Ba, Cd, Mn, Ni i Zn w szpinaku oraz Al, B, Ba, Cd, Cr, Fe, Li i Ti w sałacie wyniki badań wykazały wyższą wartość współczynników korelacji pomiędzy zawartością pierwiastków w glebie oznaczonych za pomocą 0,03 M CH₃COOH niż w 1 M HCl a zawartością tych pierwiastków w roślinach. W porównaniu z ekstrakcją 0,03 M CH₃COOH stwierdzono wyższą wartość współczynników korelacji, po oznaczeniu pierwiastków w glebie w 1 M HCl, z ich zawartością w roślinach w przypadku: Cr, Cu, Fe, Li i Sr w szpinaku oraz Ni i Pb w sałacie. Nie stwierdzono istotnego związku pomiędzy zawartością Pb i Ti w szpinaku

oraz Cu Mn, Sr and Zn w sałacie, a zawartością tych pierwiastków w glebie, oznaczanych zarówno w ekstraktach 0,03 M CH₃COOH jak i 1 M HCl.

Słowa kluczowe: 0,03 M kwas octowy, 1 M kwas solny, test Rinkisa, pierwiastki śladowe

ACKNOWLEDGEMENTS

The present study includes results of research realized within the framework of statutory activity of the department as well as grant no. N N310 3081 34: "Biofortification of selected vegetable species in iodine depending on its dose and application method".

Accepted for print – Zaakceptowano do druku: 28.06.2010