

THE INFLUENCE OF NITROGEN FERTILIZATION WITH ENTEC-26 AND AMMONIUM NITRATE ON THE CONCENTRATION OF THIRTY-ONE ELEMENTS IN CARROT (*DAUCUS CAROTA* L.) STORAGE ROOTS

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Abstract

Simultaneous application of nitrification inhibitors and nitrogen fertilizers (containing reduced forms of nitrogen (ammonium and urea) can increase soil acidification caused by these fertilizers. As a result, it can lower soil reaction (pH) and influence the content of available forms of heavy metals and trace elements. The aim of the study was to evaluate the effect of the application of: ENTEC-26 (containing 3,4-dimethylpyrazol phosphate /DMPP/ – nitrification inhibitor) and ammonium nitrate on the mineral composition of carrot storage roots. A two-year research was conducted with field cultivation of the carrot cultivar Kazan F₁. The experiment was arranged in a split-plot design with four replicates. The following combinations with different N fertilization were distinguished: 1 – control (without N fertilization), 2 – ENTEC-26 35+35, 3 – ENTEC-26 70+70, 4 – ENTEC-26 105+105, 5 – ammonium nitrate 35+35, 6 – ammonium nitrate 70+70, 7 – ammonium nitrate 105+105, where: 35+35, 70+70 and 105+105 denote nitrogen doses (kg N ha⁻¹) used for pre-plant fertilization and top-dressing, respectively. In carrot storage roots as well as in soil after carrot cultivation, concentrations of Ag, Al, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, S, Sc, Sn, Sr, Ti, Tm, Y, Yb and V were determined using the ICP-OES technique. Nutrition with nitrogen had significantly influenced the content of Co, Fe, In, Li, Mn, Ni, S, Sc, Sr, Y, Yb and V in carrot roots and this effect varied depending on the type of fertilization regime used in the experiment. No significant

impact of N fertilization was found in reference to the accumulation of Ag, Al, B, Ba, Ca, Ce, Cr, Dy, Ga, K, La, Lu, Mg, Na, P, Pb, Sn and Ti in carrot roots. In relation to the control, application of all doses of both ENTEC-26 and ammonium nitrate resulted in decreased concentration of Mg, Al, B, Ba, Ce, Fe, Ga, La, Ni, Pb, Ti, Y, V, Cr, Dy, In, Li, Lu, Sc and Yb as well as enhanced accumulation of Ca, Sr and Ag in soil after carrot cultivation. Nonetheless, the above changes in the concentration of elements in soil due to N fertilization were not reflected in their levels detected in carrot storage roots.

Keywords: nitrogen fertilization, nitrification inhibitor, DMPP, heavy metals, trace elements, rare elements.

WPLYW NAWOŻENIA AZOTEM Z ENTEC-26 I SALETRĄ AMONOWĄ NA ZAWARTOŚĆ TRZYDZIESTU JEDEN PIERWIĄTKÓW W KORZENIACH SPICHRZOWYCH MARCHWI (*DAUCUS CAROTA* L.)

Abstrakt

Aplikowanie inhibitorów nityfikacji wraz z nawozami azotowymi (zawierającymi zredukowane formy azotu: amonową i amidową) może wzmacniać zakwaszające działanie tych nawozów na glebę. W efekcie może to prowadzić do obniżenia pH oraz zmian zawartości dostępnych dla roślin form metali ciężkich i pierwiastków śladowych w glebie. Celem badań była ocena wpływu stosowania nawozów azotowych z ENTEC-26 (zawierającego inhibitor nityfikacji 3,4-dimetylopyrazolofosfat /DMPP/) i saletrą amonową na skład mineralny korzeni spichrzowych marchwi. Przeprowadzono dwuletnie badania z połową uprawą marchwi Kazan F₁. Doświadczenie założono metodą split-plot w czterech powtórzeniach. Obiektami badań były kombinacje ze zróżnicowanym nawożeniem azotem: 1 – kontrola (bez nawożenia azotem), 2 – ENTEC-26 35+35, 3 – ENTEC-26 70+70, 4 – ENTEC-26 105+105, 5 – saletra amonowa 35+35, 6 – saletra amonowa 70+70, 7 – saletra amonowa 105+105, gdzie: 35+35, 70+70 i 105+105 oznacza dawkę azotu w kg N ha⁻¹ stosowaną w nawożeniu przedsiwnym i w nawożeniu pogłównym. W korzeniach spichrzowych oraz w glebie po uprawie marchwi zawartość: Ag, Al, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, S, Sc, Sn, Sr, Ti, Tm, Y, Yb i V była oznaczana techniką ICP-OES. Nawożenie azotem miało istotny wpływ na zawartość Co, Fe, In, Li, Mn, Ni, S, Sc, Sr, Y, Yb i V w marchwi. Jednakże wpływ ten był zróżnicowany w zależności od zastosowanego sposobu nawożenia azotem w badanych kombinacjach. Nie stwierdzono natomiast istotnego oddziaływania nawożenia azotem na zawartość Ag, Al, B, Ba, Ca, Ce, Cr, Dy, Ga, K, La, Lu, Mg, Na, P, Pb, Ti i Sn w marchwi. W porównaniu z kontrolą, zastosowane nawożenie azotem we wszystkich dawkach zarówno w formie ENTEC-26, jak i saletry amonowej powodowało zmniejszenie zawartości Mg, Al, B, Ba, Ce, Fe, Ga, La, Ni, Pb, Ti, Y, V, Cr, Dy, In, Li, Lu, Sc i Yb oraz zwiększenie zawartości Ca, Sr i Ag w glebie po uprawie marchwi. Jednakże wykazane zmiany zawartości tych pierwiastków w glebie pod wpływem nawożenia azotem nie miały odzwierciedlenia w ich zawartości w korzeniach spichrzowych marchwi.

Słowa kluczowe: azot, nawożenie, inhibitor nityfikacji, DMPP, metale ciężkie, pierwiastki śladowe, pierwiastki rzadkie.

INTRODUCTION

Nitrogen fertilizers containing reduced forms of this element (ammonium, urea) belong to physiologically acid fertilizers as their application de-

creases soil pH (GĘBSKI 1998, JENTSCHKE et al. 1998, MAIER et al. 2002). Consequently, altered solubility of mineral nutrients may occur, manifested as an increased content of easily available forms of microelements (excluding molybdenum), heavy metals and trace elements in soil. As a result, enhanced uptake (and therefore accumulation) of these elements in plant tissues can be observed (MARSCHNER 1995, RODRÍGUEZ-ORTÍZ et al. 2006). However, it should be underlined that the actual influence exerted by N fertilizers depends on physicochemical properties of soil, including its buffer capacity (DIATTA, GRZEBISZ 2006).

Application of nitrification inhibitors together with nitrogen fertilizers is aimed at limiting the negative effect of NO_3^- on the environment, mainly through its reduced leaching from soil. Activity of nitrification inhibitors is generally based on processes of N-NH_4 stabilization in soil by inactivation of nitrifying microorganisms (LI et al. 2008).

Increased concentration of N-NH_4 resulting from the introduction of nitrification inhibitors can significantly enhance the acidification effect exerted by this nitrogen form on soil. Depending on physicochemical properties of soil, various changes in soil content of available forms of heavy metals and trace elements may occur. As a result, plant concentration of these elements is seriously affected, which contributes to large differences in the quality of crop.

In research on N-NH_4 stabilization in soil, numerous natural nitrification inhibitors have been tested, including *Chenopodium album* L. extract (JAFARI, KHOLDEBARIN 2002), natural essential oils (KIRAN, PATRA 2002) or *Mentha spicata* L. oil (PATRA et al. 2002). Additionally, synthetic inhibitors of this process were applied, such as nitrapyrin (ABBASI et al. 2003), dicyandiamide /DCD/ (DAVIES, WILLIAMS 1995, BLANKENAU et al. 2002, COOKSON, CORNFORTH 2002) or 3,4-dimethylpyrazol phosphate /DMPP/ (ZERULLA et al. 2001, HÄHNDEL, WISSEMEIER 2004, GIOACCHINI et al. 2006). The above compounds differ in their power to depress the nitrification rate as well as in the spectrum of activities towards soil microflora.

The negative impact of high concentrations of heavy metals manifested as a limited nitrification rate is relatively well documented (ROTHER et al. 1982, CELA, SUMER 2002). In contrast, acknowledging the influence of nitrification inhibitors on the solubility of available forms of mineral elements in soil requires thorough research. The recognition of the effect exerted by N fertilizers containing nitrification inhibitors on the mineral composition of plants is particularly important for obtaining high quality of crops. The mineral composition of consumed plant food has direct influence on human health. For this reason, an objective assessment of the activity of nitrification inhibitors is essential for vegetable production, including carrots processed into baby food, as carrot is one of the main components used in this kind of products.

The influence of nitrogen fertilization on soil environment and mineral composition of plants is also determined by many other factors related with physicochemical properties of soil, e.g. soil type, texture and redox potential, the content of organic matter (GĘBSKI 1998), cation exchange capacity, base saturation ratio as well as soil content of Ca, Mg and heavy metals (SADY, ROŻEK 2002). There are some interesting results of long-term studies on carrot cultivation on soils with differentiated physicochemical properties (SADY et al. 1999, 2000, SADY, ROŻEK 2002, SMOLEŃ, SADY 2006). The lowest rate of heavy metal (cadmium) accumulation in carrot storage roots was noted in the case of plants grown on soils characterized by: $\text{pH}_{\text{KCl}} > 7.0$, base saturation ratio $V > 98\%$ as well as Ca content exceeding $2,900 \text{ mg dm}^{-3}$. Carrot cultivation on soils with similar physicochemical properties provides storage roots with a relatively low level of heavy metal (Cd and Pb) accumulation, which means they can be used for production of baby food. Such food products must contain significantly less cadmium and lead than those dedicated to adult consumers. Baby food manufacturing plants located in south-eastern Poland use carrots cultivated only on this type of soil, as demonstrated by the unpublished data obtained from direct interviews and long-term field studies conducted in this part of the country (SADY et al. 1999, 2000, SADY, ROŻEK 2002, SMOLEŃ, SADY 2006). The above finding encouraged us to undertake the present study on carrot cultivation on alkaline soil with high calcium content.

The problem of nitrogen fertilization affecting soil environment and mineral composition of plants (defined as plant nutrition and heavy metal accumulation) has been relatively well documented. Nevertheless, previous studies rarely included the effect of N application on changes in soil level of trace elements and their uptake by plants. The importance of numerous trace elements to living organisms is yet to be revealed. Recognition of their levels in plants tissues as well as factors affecting their accumulation can significantly broaden our current scope of knowledge.

The aim of this work has been to evaluate the influence of the application of nitrogen fertilizer ENTEC-26 (containing nitrification inhibitor DMPP), in association with ammonium nitrate, on the mineral composition of carrot storage roots. An attempt has been made to comprehensively assess the effect of the above fertilizers on the content of macro- and microelements, heavy metals and trace elements (including rare earth elements) in carrot roots.

MATERIAL AND METHODS

Plant material and treatments

In 2004-2005, a field experiment involving cv. Kazan F₁ carrot was conducted in Trzciana (50°06' N, 21°85' E in south-eastern Poland). Each year carrot plants grew on a different site within the same soil complex. Carrot was cultivated in a three-year crop rotation including sugar beets (1st year), winter wheat (2nd year) and carrot (3rd year). Carrot plants were grown on raised beds, 140 cm wide and 30 cm high, on which seeds were sown in three rows, spaced 30 cm apart, at a rate of 45 seeds m⁻¹ (1 million of seeds per hectare). The seeds were sown on 24 April 2004 and 30 April 2005.

The experiment was arranged in a split-plot design. The following combinations with different nitrogen fertilization were distinguished: 1 – control (without nitrogen fertilization), 2 – ENTEC-26 35+35 kg N ha⁻¹, 3 – ENTEC-26 70+70 kg N ha⁻¹, 4 – ENTEC-26 105+105 kg N ha⁻¹, 5 – ammonium nitrate (NH₄NO₃ 35+35 kg N ha⁻¹), 6 – ammonium nitrate (NH₄NO₃ 70+70 kg N ha⁻¹), 7 – ammonium nitrate (NH₄NO₃ 105+105 kg N ha⁻¹), where 35+35, 70+70 and 105+105 denote nitrogen doses applied for pre-plant fertilization and top-dressing, respectively. Solid nitrogen fertilizer was added to soil in the form of ammonium nitrate (Zakłady Azotowe in Puławy, Poland) and ENTEC-26 as COMPO (GmbH & Co. KG, Germany). ENTEC-26 fertilizer contains 26% N (7.5% N-NO₃, 18.5% N-NH₄), 13% S and 0.8% nitrification inhibitor DMPP. Pre-sowing nitrogen fertilization was conducted directly before bed formation, whereas top dressing was carried out at canopy closure. Each experimental treatment was randomized in four replicates on 2.4 m×6 m (14.4 m²) plots. The total area used for experiment was 403 m².

Carrots were harvested on 24 September 2004 and 8 September 2005. At harvest, samples of about 5 kg of carrot storage roots were collected in four replications (i.e. from each plot) for laboratory analyses.

A detailed description of the course of carrot cultivation (together with the climatic conditions) as well as yield and the results of chemical analysis of storage roots and soil (prior to and after carrot cultivation) has been presented in previous works (SMOLEŃ, SADY 2007, 2008 a, 2009a, b, 2011).

Plant analysis

Each year, shredded plant material (carrot storage roots) was dried at 70°C, ground and mineralized in 65% super pure HNO₃ (Merck no. 100443.2500) in a CEM MARS-5 Xpress microwave oven (PASŁAWSKI, MIGASZEWSKI 2006). Certified material, i.e. peach leaves (CRM 3 1547), was mineralized in the same way. Concentrations of Ag, Al, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, S, Sc, Sn, Sr, Ti, Tm, Y, Yb and V in mineralized plant samples were determined using the ICP-OES technique.

Soil analysis

Soils samples from two layers (0-30 cm and 30-60 cm) were collected on two dates – in spring prior to the start of the experiment as well as during carrot harvesting. In spring, eight samples were collected at random from the total area of the experiment. During carrot harvest, soil samples were collected individually for each nitrogen fertilization treatment. Samples were collected from 0-30 cm and 30-60 cm soil layers because the uptake of mineral nutrients by carrot plants occurs in both arable layer (0-30 cm, from which raised beds are formed) and lower soil layers (30-60 cm), a finding reported by WESTERVELD et al. (2006 a, b).

Before the experiment, the following tests were made to characterize the type of soil: soil texture was analysed using Casagrande method, modified by Pruszyński (KOMORNICKI et al. 1991), organic matter content was assessed by Tiurin method, modified by Oleksynowa (KOMORNICKI et al. 1991), and pH was determined with a potentiometer (1:2 v/v soil in 1 M KCl and in H₂O). The content of macronutrients (N-NH₄, N-NO₃, P, K, Mg, Ca) was determined after soil extraction with 0.03 M acetic acid (NOWOSIELSKI 1988). Soil concentration of N-NO₃ and N-NH₄ was assayed using the micro-distilling method (NOWOSIELSKI 1988), while K, Mg, Ca were determined by the AAS technique (OSTROWSKA et al. 1991). The phosphorus level was determined using the vanadium-molybdenum method (NOWOSIELSKI 1988). Soil sorption properties were characterized by hydrolytic acidity (Ha) in 1 M (CH₃COOH)₂Ca with pH = 8.2 using Kappen method (OSTROWSKA et al. 1991), sum of exchangeable basic cations (abbreviated as S, $S = S_{Na} + S_K + S_{Ca} + S_{Mg}$) after soil extraction using 1 M NH₄Cl (KOCIAŁKOWSKI et al. 1984) as well as cation exchange capacity (abbreviated as CEC, $CEC = Ha + S$) and base saturation ratio V% ($V\% = S \cdot 100 : T$).

Soil samples collected after carrot cultivation were dried in open air, ground and passed through a 1 mm mesh sieve. Subsequently, soil extraction with 1 M HCl was carried out according to Rinkis method (GORLACH et al. 1999). The extracts were assayed for their content of the same elements as carrot roots with the ICP-OES technique. Soil extraction with 1 M HCl is commonly applied for analysis of micronutrients in soil.

Soil samples collected before carrot cultivation were analyzed to determine both physicochemical properties of soil and fertilization requirements of plants for mineral nutrients (N, P, K, Mg and Ca analysis after soil extraction with 0.03 M acetic acid) according to methods commonly applied in vegetable production in Poland, that is mineral analysis based on extraction with 0.03 M acetic acid (NOWOSIELSKI 1988).

Mineral composition of soil after carrot cultivation was assayed using the universal extraction solution of 1 M HCl. In the diagnostic practice of soil chemical properties, the preferred methods are the ones which enable researchers to determine available forms of numerous mineral nutrients in a single soil extract (SMOLEŃ et al. 2010a, b). Soil extraction with 1 M HCl

was applied in order to evaluate the effect of N fertilization on the content of easily assimilable forms of the tested elements in soil. The aim of this procedure was to determine the geochemical background (concentration of elements in soil) for the influence of nitrogen application on the content of the tested elements in carrot roots.

Previous studies (SMOLEŇ et al. 2010a) revealed the applicability of this method to the assessment of the relation between the soil content of Co, Fe, Mn, Mo and Pb in 0-30 cm, 30-60 cm and 60-90 cm layers and accumulation of these elements in carrot storage roots (on the basis of correlation coefficient values).

Determination of elements in carrot and soil samples

The content of thirty-one elements (Ag, Al, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, S, Sc, Sn, Sr, Ti, Tm, Y,

Table 1
Results of determination of elements in certified reference material – peach leaves (CRM 3 1547)

Concentration of elements	(% d.w.)				
	Ca	K	Mg	P	S
Certified value	1.56	2.43	0.432	-	0.2*
Obtained value	1.64	2.27	0.46	0.15	0.18
	(mg kg ⁻¹ d.w.)				
	Ag	Al	B		
Certified value	-	249	29		
Obtained value	0.39	192.43	27.45		
	Ba	Ce	Co	Cr	
Certified value	124	10*	0.07*	1*	
Obtained value	113.71	11.21	0.08	0.99	
	Dy	Fe	Ga	In	
Certified value	-	220*	-	-	
Obtained value	1.56	191.38	3.66	0.18	
	La	Li	Lu	Mn	Na
Certified value	9*	-	-	98	24
Obtained value	8.99	0.06	0.016	91.26	24.68
	Ni	Pb	Sc	Sr	Sn
Certified value	0.69	0.87	0.04*	53	<0.2*
Obtained value	0.98	0.91	0.022	45.99	0.0035
	Ti	Tm	Y	Yb	V
Certified value	-	-	-	-	0.37
Obtained value	11.00	0.0021	2.68	0.103	0.20

*approximate value (not certified)

Yb and V) in carrot and soil samples was determined with the use of a ICP-OES spectrometer (Prodigy Teledyne Leeman Labs USA). The ICP-OES instrument was calibrated using Merck's ICP multi-element standards nos VI and XVI, Inorganic Ventures ICP single element standards of Ca, K, Mg, Na, P and S as well as standard no. 69 for a group of rare elements. Analysis of the certified material (CRM 3 1547 – peach leaves) was conducted using the same emission and calibration lines as for carrot samples. The results of determination of elements in the certified material are presented in Table 1.

Soil characteristics

In both years, the 0-30 cm and the 30-60 cm soil layers were classified as heavy soils (Table 2). In 2004-2005, all the soil sites had a similar organic matter content in both layers. Soil reaction pH_{KCl} on all sites ranged from 7.15 to 7.35, while $\text{pH}_{\text{H}_2\text{O}}$ was 7.55-7.80. The average content of mineral nitrogen ($\text{N-NH}_4 + \text{N-NO}_3$) in the 0-60 cm layers in spring (before the experiment) was 273 and 246 kg N ha⁻¹ in 2004 and 2005, respectively. In both years, the soil contained comparable levels of phosphorus. The level of easily soluble forms of K, Mg, and Ca in the tested soil layers differed between the two years. In 2005, the soil had a slightly higher potassium content than in 2004. A relatively high concentration of magnesium in soil was observed in 2004, whereas in 2005, the soil had a high calcium content. Cation exchange capacity of the soil remained similar in both years and base saturation ratio (V %) surpassed 90%.

Table 2

Physical and chemical properties of 0-30 and 30-60 cm soil layers prior to the start of experiments in 2004-2005

Characteristics	2004		2005	
	0-30 cm	30-60 cm	0-30 cm	30-60 cm
Soil texture class	silty clay	silty clay	silty clay	silty clay
Organic matter (%)	2.20	1.33	2.26	1.50
pH_{KCl}	7.16	7.15	7.35	7.32
$\text{pH}_{\text{H}_2\text{O}}$	7.80	7.75	7.55	7.70
N-NH_4 (mg dm ⁻³)	12.3	10.5	21.0	7.0
N-NO_3 (mg dm ⁻³)	33.3	35.0	33.3	21.0
P (mg dm ⁻³)	50.6	50.5	53.1	43.2
K (mg dm ⁻³)	35.8	14.7	128.7	64.6
Mg (mg dm ⁻³)	81.0	83.2	61.5	63.3
Ca (mg dm ⁻³)	6 433.3	6 613.3	7 258.0	7 352.5
Cation exchange capacity (CEC cmol kg ⁻¹)	14.7	18.0	16.6	18.0
Saturation of the sorption complex with alkaline elements (%)	94.9	93.6	96.9	96.7

Statistical analysis

The results were statistically verified with the ANOVA module of Statistica 8.0 PL at $p < 0.05$. The significance of differences was calculated using Duncan's test.

RESULTS

Soil fertilization with nitrogen had a significant influence on the content of S, Fe, Mn, Ni and Sr (Table 3) as well as Co, In, Li, Sc, Y, Yb and V (Table 4) in carrot storage roots. No effect of N nutrition was observed in respect of the concentration of Ca, K, Mg, Na, P, Al, B, Ba, Ga, Ti, Ag, Ce, Cr, Dy, La, Lu, Pb and Sn in carrot (Tables 3 and 4).

In comparison to the control, nitrogen fertilization, both in the form of ENTEC-26 and ammonium nitrate and in all the applied doses, contributed to a comparable increase in the accumulation of S, Mn and Sr in carrot roots. A similar tendency was found for Fe but the highest content of this element was noted in roots of carrot plants fertilized with ENTEC-26 in the dose of 35+35 kg N ha⁻¹.

A significant increase in the accumulation of Co (versus the control) was noted only in carrot fertilized with ENTEC-26 in the dose of 35+35 kg N ha⁻¹ (Table 4). It is worth mentioning that fertilization with higher amounts of ENTEC-26 (70+70 as well as 105+105 kg N ha⁻¹) significantly reduced the Co concentration in carrot in comparison to the application of 35+35 kg N ha⁻¹. In the case of ammonium nitrate, storage roots of carrot fertilized with 105+105 kg N ha⁻¹ contained significantly more cobalt than plants fertilized with lower doses of this nitrogen source (35+35 as well as 70+70 kg N ha⁻¹). Roots of carrot fertilized with 105+105 kg N ha⁻¹ dose of ammonium nitrate accumulated the highest amount of indium while plants grown in the presence of 35+35 kg N ha⁻¹ were characterized by the highest concentration of lithium. In comparison to the control, a significant decrease in the content of scandium was noted in plants fertilized with the highest dose of ENTEC-26 (105+105 kg N ha⁻¹). In the case of Sc and Yb, decreased accumulation of the former and increased one of the latter element were observed along with an increasing dose of ENTEC-26. The highest concentrations of Sc, Y and Yb were determined in storage roots of carrot grown in the presence of the lowest level of ammonium nitrate (35+35 kg N ha⁻¹). In comparison to the control, reduced accumulation of yttrium was noted in carrot storage roots fertilized with ENTEC-26 in the dose of 70+70 or 105+105 kg N ha⁻¹. The applied N fertilization, both in the form of ENTEC-26 and ammonium nitrate, contributed to a general decrease in the vanadium content in roots. A significant change in the accumulation of this element was observed after the application of 70+70 and 105+105 kg N ha⁻¹

Table 3

Concentration of Ca, K, Mg, Na, P, S, Al, B, Ba, Fe, Ga, Mn, Ni, Sr and Ti in carrot storage roots depending on nitrogen fertilization – means from 2004-2005

Combinations	(% d.w.)					
	Ca	K	Mg	Na	P	S
Control	0.45	2.61	0.13	0.56	0.42	0.14 <i>a</i>
ENTEC-26 35+35 kg N ha ⁻¹	0.48	3.14	0.14	0.57	0.47	0.17 <i>b</i>
ENTEC-26 70+70 kg N ha ⁻¹	0.53	3.23	0.16	0.63	0.51	0.19 <i>b</i>
ENTEC-26 105+105 kg N ha ⁻¹	0.49	3.06	0.14	0.56	0.47	0.18 <i>b</i>
NH ₄ NO ₃ 35+35 kg N ha ⁻¹	0.51	3.40	0.15	0.69	0.51	0.18 <i>b</i>
NH ₄ NO ₃ 70+70 kg N ha ⁻¹	0.50	3.10	0.15	0.58	0.48	0.16 <i>ab</i>
NH ₄ NO ₃ 105+105 kg N ha ⁻¹	0.52	3.34	0.15	0.60	0.51	0.17 <i>b</i>
Test <i>F</i> for fertilization	n.s.	n.s.	n.s.	n.s.	n.s.	*
	(mg kg ⁻¹ d.w.)					
Control	43.74	31.43	19.62	44.59 <i>a</i>	1.77	5.88 <i>a</i>
ENTEC-26 35+35 kg N ha ⁻¹	36.89	34.38	18.41	50.74 <i>ab</i>	1.57	7.44 <i>b</i>
ENTEC-26 70+70 kg N ha ⁻¹	30.45	36.60	17.85	51.97 <i>ab</i>	1.59	8.20 <i>b</i>
ENTEC-26 105+105 kg N ha ⁻¹	31.88	35.24	15.98	48.12 <i>ab</i>	1.42	7.32 <i>b</i>
NH ₄ NO ₃ 35+35 kg N ha ⁻¹	47.50	36.04	19.30	63.24 <i>c</i>	1.66	7.86 <i>b</i>
NH ₄ NO ₃ 70+70 kg N ha ⁻¹	36.02	34.31	16.36	56.53 <i>bc</i>	1.50	7.71 <i>b</i>
NH ₄ NO ₃ 105+105 kg N ha ⁻¹	40.28	36.94	17.58	57.08 <i>bc</i>	1.52	8.11 <i>b</i>
Test <i>F</i> for fertilization	n.s.	n.s.	n.s.	*	n.s.	*
			Ni	Sr	Ti	
Control			2.87 <i>b</i>	16.71 <i>a</i>	3.06	
ENTEC-26 35+35 kg N ha ⁻¹			3.31 <i>b</i>	43.12 <i>b</i>	2.55	
ENTEC-26 70+70 kg N ha ⁻¹			2.31 <i>ab</i>	41.89 <i>b</i>	3.03	
ENTEC-26 105+105 kg N ha ⁻¹			1.06 <i>a</i>	45.24 <i>b</i>	2.20	
NH ₄ NO ₃ 35+35 kg N ha ⁻¹			1.11 <i>a</i>	46.91 <i>b</i>	3.27	
NH ₄ NO ₃ 70+70 kg N ha ⁻¹			1.11 <i>a</i>	45.99 <i>b</i>	2.98	
NH ₄ NO ₃ 105+105 kg N ha ⁻¹			1.18 <i>a</i>	43.03 <i>b</i>	3.47	
Test <i>F</i> for fertilization			*	*	n.s.	

Test *F*: * means are significantly different, n.s. – not significant.

Means followed by the same letters are not significantly different at $p < 0.05$.

Table 4

Concentration of Ag, Ce, Co, Cr, Dy, In, La, Li, Lu, Pb, Sc, Sn, Tm, Y, Yb and V in carrot storage roots depending on nitrogen fertilization – means from 2004-20055

Combinations	(µg kg ⁻¹ d.w.)					
	Ag	Ce	Co	Cr	Dy	In
Control	99.02	991.05	19.35 <i>ab</i>	208.39	43.49	185.82 <i>abc</i>
ENTEC-26 35+35 kg N ha ⁻¹	98.36	1029.99	49.10 <i>c</i>	267.70	51.15	137.61 <i>ab</i>
ENTEC-26 70+70 kg N ha ⁻¹	137.73	1065.73	13.03 <i>ab</i>	210.44	45.64	199.89 <i>ab</i>
ENTEC-26 105+105 kg N ha ⁻¹	104.01	1026.78	13.03 <i>ab</i>	191.57	50.62	121.80 <i>a</i>
NH ₄ NO ₃ 35+35 kg N ha ⁻¹	104.02	976.28	5.40 <i>a</i>	224.98	56.92	168.68 <i>abc</i>
NH ₄ NO ₃ 70+70 kg N ha ⁻¹	94.54	1002.30	9.71 <i>a</i>	189.29	51.13	120.48 <i>a</i>
NH ₄ NO ₃ 105+105 kg N ha ⁻¹	92.81	990.65	23.98 <i>b</i>	310.73	50.25	214.85 <i>c</i>
Test <i>F</i> for fertilization	n.s.	n.s.	*	n.s.	n.s.	*
	La	Li	Lu	Pb	Sc	Sn
Control	109.32	49.45 <i>a</i>	1.33	77.64	2.81 <i>bc</i>	1.22
ENTEC-26 35+35 kg N ha ⁻¹	114.69	58.64 <i>a</i>	1.41	76.52	2.66 <i>bc</i>	0.89
ENTEC-26 70+70 kg N ha ⁻¹	93.32	50.81 <i>a</i>	0.65	19.03	1.17 <i>ab</i>	0.80
ENTEC-26 105+105 kg N ha ⁻¹	105.01	44.79 <i>a</i>	1.57	59.10	0.88 <i>a</i>	1.43
NH ₄ NO ₃ 35+35 kg N ha ⁻¹	113.43	75.66 <i>b</i>	1.54	70.84	4.16 <i>c</i>	1.25
NH ₄ NO ₃ 70+70 kg N ha ⁻¹	107.71	56.44 <i>a</i>	1.26	68.60	1.50 <i>ab</i>	0.94
NH ₄ NO ₃ 105+105 kg N ha ⁻¹	117.25	56.59 <i>a</i>	1.60	72.82	2.25 <i>ab</i>	0.79
Test <i>F</i> for fertilization	n.s.	*	n.s.	n.s.	*	n.s.
		Tm	Y	Yb	V	
Control		0.85	11.75 <i>c</i>	2.90 <i>bc</i>	93.32 <i>c</i>	
ENTEC-26 35+35 kg N ha ⁻¹		1.38	9.74 <i>bc</i>	1.22 <i>a</i>	73.66 <i>abc</i>	
ENTEC-26 70+70 kg N ha ⁻¹		0.33	5.45 <i>a</i>	1.97 <i>ab</i>	52.82 <i>a</i>	
ENTEC-26 105+105 kg N ha ⁻¹		3.77	7.79 <i>ab</i>	3.85 <i>cd</i>	62.60 <i>ab</i>	
NH ₄ NO ₃ 35+35 kg N ha ⁻¹		7.64	15.27 <i>d</i>	5.32 <i>d</i>	83.54 <i>bc</i>	
NH ₄ NO ₃ 70+70 kg N ha ⁻¹		<l.d.	10.33 <i>bc</i>	2.59 <i>abc</i>	58.30 <i>ab</i>	
NH ₄ NO ₃ 105+105 kg N ha ⁻¹		<l.d.	11.99 <i>c</i>	3.99 <i>cd</i>	77.85 <i>abc</i>	
Test <i>F</i> for fertilization		-	*	*	*	

Test *F*: * means are significantly different, n.s. – not significant.

Means followed by the same letters are not significantly different at $p < 0.05$.

of ENTEC-26 as well as 70+70 kg N ha⁻¹ of ammonium nitrate. Nitrogen fertilization had a variable effect on thulium accumulation in carrot. The highest concentration of Tm was found in roots fertilized with ammonium nitrate in the dose of 35+35 kg N ha⁻¹. In carrot roots treated with higher doses of this nitrogen compound (70+70 and 105+105 kg N ha⁻¹), the content of thulium was below its detectability on a ICP-OES spectrometer.

It should be mentioned that nitrogen application resulted in increased accumulation of Cu by carrot storage roots (when compared to the control plants) except the combination with ENTEC-26 35+35 kg N ha⁻¹. More detailed results were presented previously (SMOLEŇ, SADY 2007). This level of nitrogen supply did not affect Cd and Zn concentrations in carrot storage roots (SMOLEŇ, SADY 2007).

In the soil after carrot cultivation, significant variation was observed in concentrations of Ca, K, Mg, S, Al, B, Ba, Ce, Co, Fe, Ga, La, Mn, Ni, Pb, Sr, Ti, Y, V, Ag, Cr, Dy, In, Li, Lu, Sc and Yb, which was related to the applied nitrogen nutrition (in soil layers 0-30 cm and 30-60 cm as well as for means 0-60 cm – Tables 5, 6 and 7). No significant changes were noticed in the soil content of Na, P, Tm (in soil layers 0-30 cm and 30-60 cm as well as for means 0-60 cm) and Sn (in the 0-30 cm layer as well as for means 0-60 cm) in all the tested combinations. In comparison to the control, nitrogen fertilization (regardless of its dose and used compound) induced lower levels of Mg, Al, B, Ba, Ce, Fe, Ga, La, Ni, Pb, Ti, Y, V, Cr, Dy, In, Li, Lu, Sc and Yb as well as higher accumulation of Ca, Sr and Ag in soil (in both soil layers and means 0-60 cm – Tables 5, 6 and 7) after carrot cultivation. It should be underlined that the Ni content in the 30-60 cm layer from the fertilization variant ENTEC-26 105+105 kg N ha⁻¹ was comparable to the control. In the case of Sn, a significant influence of N application was noted only in the 30-60 cm soil layer. Nonetheless, the level of Sn in soil fertilized with nitrogen was similar to the control value. The highest content of tin was found in the 30-60 cm layer of soil fertilized with NH₄NO₃ 70+70 kg N ha⁻¹.

Along with an increasing dose of ENTEC-26, a significant rise in the soil content of sulphur was found. In the soil supplied with ammonium nitrate (in all the tested doses), the S concentration remained comparable to the control.

In respect of potassium, application of higher N doses in both tested form (ENTECC-26 and ammonium nitrate) resulted in reduced soil accumulation of this element when compared to fertilization with 35+35 kg N ha⁻¹. The lowest level of cobalt in soil was noted due to fertilization with ENTEC-26 and ammonium nitrate in the concentration of 70+70 kg N ha⁻¹. In comparison to the control, a significant decrease in the soil content of manganese was observed for the 35+35 kg N ha⁻¹ dose of ENTEC-26 as well as ammonium nitrate in the doses of 70+70 and 105+105 kg N ha⁻¹.

Table 5
Concentrations of Ca, K, Mg, Na, P, S, Al, B, Ba and Ce in soil after carrot cultivation depending on pre-plant and top dressing nitrogen fertilization - means from years 2004-2005

Soil layer	Combinations	(mg kg ⁻¹ soil)									
		Ca	K	Mg	Na	P	S	Al	B	Ba	Ce
0-30 cm	control	14185.7 a	132.2 d	866.4 b	31.6	390.5	37.2 a	964.1 c	2.6 d	29.5 c	9.5 c
	ENTEC-26 35+35 kg N ha ⁻¹	15 728.8 bc	143.9 e	673.9 a	32.6	374.1	37.2 a	697.8 ab	2.0 c	26.2 b	8.3 b
	ENTEC-26 70+70 kg N ha ⁻¹	16 614.8 d	122.1 b	674.9 a	33.2	344.1	38.1 a	676.2 a	1.8 ab	25.4 a	8.2 ab
	ENTEC-26 105+105 kg N ha ⁻¹	16 262.0 cd	105.7 a	668.5 a	31.6	339.2	70.8 b	708.9 bc	1.8 b	26.1 b	8.1 ab
	NH ₄ NO ₃ 35+35 kg N ha ⁻¹	16 693.0 d	127.0 c	678.6 a	32.0	357.4	35.7 a	677.1 a	1.8 ab	25.9 ab	8.2 ab
	NH ₄ NO ₃ 70+70 kg N ha ⁻¹	15 636.2 b	105.2 a	666.9 a	33.2	371.9	39.4 a	694.5 ab	1.7 a	25.8 ab	8.1 a
30-60 cm	NH ₄ NO ₃ 105+105 kg N ha ⁻¹	16 127.6 bcd	124.0 bc	678.9 a	33.8	349.8	36.8 a	690.3 ab	1.8 b	26.4 b	8.3 b
	test <i>F</i> for fertilization	*	*	*	n.s.	n.s.	*	*	*	*	*
	control	15 312.0 a	84.2 c	1002.3 d	32.8	226.1	29.3 a	1001.6 c	1.3 e	27.1 e	9.0 e
	ENTEC-26 35+35 kg N ha ⁻¹	18 699.0 b	99.3 d	756.6 c	34.7	232.0	37.0 c	705.9 b	1.1 cd	22.8 b	7.8 bc
	ENTEC-26 70+70 kg N ha ⁻¹	19 780.9 d	73.7 b	713.0 a	35.8	243.7	50.4 d	665.9 a	0.8 a	22.4 ab	7.7 bc
	ENTEC-26 105+105 kg N ha ⁻¹	19 064.2 bc	76.6 b	733.1 b	36.7	254.3	52.1 d	713.6 b	1.1 d	23.8 c	7.9 cd
0-30 cm	NH ₄ NO ₃ 35+35 kg N ha ⁻¹	19 314.7 cd	75.6 b	735.6 b	34.4	261.4	31.1 ab	726.9 b	1.0 b	24.5 d	8.0 d
	NH ₄ NO ₃ 70+70 kg N ha ⁻¹	18 702.4 b	63.4 a	710.4 a	34.9	263.3	31.6 ab	657.8 a	0.8 a	22.0 a	7.5 a
	NH ₄ NO ₃ 105+105 kg N ha ⁻¹	18 622.6 b	72.1 b	735.5 b	36.8	254.1	27.6 a	703.7 b	1.0 bc	23.6 c	7.7 b
	test <i>F</i> for fertilization	*	*	*	n.s.	*	*	*	*	*	*

Test *F*: * means are significantly different, n.s. – not significant.
Means followed by the same letters are not significantly different at $p < 0.05$.

Table 6

Concentrations of Co, Fe, Ga, La, Mn, Ni, Pb, Sr, Ti, Y and V in soil after carrot cultivation depending on pre-plant and top dressing nitrogen fertilization – means from years 2004-2005

Soil layer	Combinations	(mg kg ⁻¹ soil)										
		Co	Fe	Ga	La	Mn	Ni	Pb	Sr	Ti	Y	V
0-30 cm	control	2.29 c	2365.0 c	2.15 b	3.91 c	276.4 b	4.13 c	10.02 c	32.2 a	5.79 d	4.57 d	5.0 d
	ENTEC-26 35+35 kg N ha ⁻¹	2.15 b	1854.0 a	1.86 a	3.35 b	266.8 a	3.70 b	8.16 b	61.1 c	4.62 ab	3.89 c	3.8 bc
	ENTEC-26 70+70 kg N ha ⁻¹	2.09 ab	1922.7 ab	1.93 a	3.27 ab	266.7 a	3.57 a	7.68 a	59.6 c	4.76 bc	3.81 ab	3.7 a
	ENTEC-26 105+105 kg N ha ⁻¹	2.15 b	1934.2 b	1.92 a	3.27 ab	268.5 ab	3.71 b	8.21 b	63.2 d	4.80 c	3.81 ab	3.9 c
	NH ₄ NO ₃ 35+35 kg N ha ⁻¹	2.14 b	1891.8 ab	1.91 a	3.31 ab	268.0 a	3.64 ab	8.02 ab	63.0 d	4.61 a	3.81 ab	3.7 a
	NH ₄ NO ₃ 70+70 kg N ha ⁻¹	2.11 ab	1890.2 ab	1.87 a	3.23 a	262.2 a	3.65 ab	8.46 b	57.7 b	4.66 abc	3.76 a	3.8 ab
30-60 cm	NH ₄ NO ₃ 105+105 kg N ha ⁻¹	2.15 b	1873.3 ab	1.91 a	3.32 b	268.1 a	3.73 b	8.17 b	62.9 d	4.61 a	3.86 ab	3.8 ab
	test <i>F</i> for fertilization	*	*	*	*	*	*	*	*	*	*	*
	control	2.11 ab	2503.7 e	2.47 d	3.63 d	251.6 ab	3.86 d	6.77 e	34.8 a	8.69 d	4.32 e	4.2 e
	ENTEC-26 35+35 kg N ha ⁻¹	2.11 ab	2073.6 b	2.09 ab	3.09 b	248.7 ab	3.52 bc	5.60 ab	64.1 cd	6.26 b	3.60 bc	3.2 bc
	ENTEC-26 70+70 kg N ha ⁻¹	2.07 a	2160.2 c	2.12 ab	3.03 b	253.0 ab	3.38 a	5.49 a	63.2 c	6.28 b	3.51 b	3.1 ab
	ENTEC-26 105+105 kg N ha ⁻¹	2.23 c	2150.4 c	2.15 b	3.10 b	269.3 c	3.76 d	6.40 de	66.9 e	6.30 b	3.62 c	3.4 d
0-30 cm	NH ₄ NO ₃ 35+35 kg N ha ⁻¹	2.14 b	2382.5 d	2.31 c	3.18 c	256.9 bc	3.56 c	5.94 bc	71.1 f	7.05 c	3.72 d	3.4 d
	NH ₄ NO ₃ 70+70 kg N ha ⁻¹	2.06 a	2080.4 b	2.05 a	2.94 a	254.0 ab	3.44 ab	5.63 ab	60.5 b	6.01 a	3.41 a	3.0 a
	NH ₄ NO ₃ 105+105 kg N ha ⁻¹	2.07 a	1999.2 a	2.08 ab	3.07 b	247.0 a	3.54 bc	6.19 cd	65.6 de	6.30 b	3.57 bc	3.2 c
	test <i>F</i> for fertilization	*	*	*	*	*	*	*	*	*	*	*

Test *F*: * means are significantly different, n.s. – not significant.

Means followed by the same letters are not significantly different at $p < 0.05$.

Table 7

Concentrations of Ag, Cr, Dy, In, Li, Lu, Sc, Sn, Tm and Yb in soil after carrot cultivation depending on pre-plant and top dressing nitrogen fertilization – means from years 2004-2005

Soil layer	Combinations	(µg kg ⁻¹ soil)									
		Ag	Cr	Dy	In	Li	Lu	Sc	Sn	Tm	Yb
0-30 cm	control	164.8 a	1100.3 c	487.5 d	379.8 c	858.0 c	93.5 c	39.0 c	153.8	39.3	372.3 b
	ENTEC-26 35+35 kg N ha ⁻¹	188.8 bc	925.0 b	360.8 c	294.3 abc	641.0 a	77.0 abc	29.8 a	166.8	35.5	313.0 a
	ENTEC-26 70+70 kg N ha ⁻¹	190.5 bc	897.8 ab	324.3 a	242.0 a	637.3 a	76.8 ab	32.3 b	155.5	37.8	307.3 a
	ENTEC-26 105+105 kg N ha ⁻¹	189.0 bc	907.3 b	332.0 a	280.3 ab	680.0 b	77.0 abc	30.5 ab	177.8	34.8	309.8 a
	NH ₄ NO ₃ 35+35 kg N ha ⁻¹	188.5 bc	904.5 b	325.0 a	299.5 abc	638.0 a	76.5 a	31.5 ab	196.0	36.0	307.8 a
	NH ₄ NO ₃ 70+70 kg N ha ⁻¹	180.5 b	913.0 b	334.8 a	313.0 abc	658.5 bc	76.0 a	30.0 a	149.3	40.3	305.0 a
30-60 cm	NH ₄ NO ₃ 105+105 kg N ha ⁻¹	194.0 c	907.3 b	349.0 b	291.3 abc	642.3 a	76.0 a	30.8 ab	148.0	40.8	312.3 a
	test <i>F</i> for fertilization	*	*	*	*	*	*	*	n.s.	n.s.	*
	control	176.5 a	1100.5 e	412.8 d	387.5 c	1036.8 e	94.8 d	65.5 e	193.5 ab	41.8	358.8 e
	ENTEC-26 35+35 kg N ha ⁻¹	210.0 bc	840.5 ab	244.8 c	293.8 ab	768.5 bc d	79.3 ab	52.0 b	96.3 a	36.5	296.5 bc
	ENTEC-26 70+70 kg N ha ⁻¹	218.5 c	844.5 ab	199.8 a	307.5 ab	746.0 ab	79.5 bc	55.3 c	129.8 ab	38.8	290.0 b
	ENTEC-26 105+105 kg N ha ⁻¹	214.3 c	869.8 bc	222.8 b	323.3 ab	775.8 cd	79.5 b	48.3 a	152.3 ab	44.8	298.3 cd
0-30 cm	NH ₄ NO ₃ 35+35 kg N ha ⁻¹	216.3 c	908.8 d	226.3 b	362.0 abc	794.0 d	86.5 c	58.3 d	140.8 ab	39.0	308.8 d
	NH ₄ NO ₃ 70+70 kg N ha ⁻¹	217.5 c	829.8 a	196.0 a	326.5 ab	734.5 a	77.3 ab	48.5 a	373.8 b	38.5	282.5 a
	NH ₄ NO ₃ 105+105 kg N ha ⁻¹	201.0 b	848.0 ab	237.5 c	281.0 a	761.8 bc	76.8 a	47.3 a	105.8 a	39.5	292.3 bc
	test <i>F</i> for fertilization	*	*	*	*	*	*	*	*	n.s.	*

Test *F*: * means are significantly different, n.s. – not significant.

Means followed by the same letters are not significantly different at $p < 0.05$.

DISCUSSION

One of the major factors influencing the mineral uptake by plants is soil pH. Fluctuations in this parameter stimulated by the use of mineral fertilizers can affect the level of macronutrient uptake by plants (MARSCHNER 1995). In this context, it should be underlined that the application of physiologically acid nitrogen fertilizers tested in this experiment did not significantly affect soil pH (data published previously, SMOLEŇ, SADY 2007, 2011). Soil pH after carrot cultivation was above of 7.5 (means from 2004 and 2005 for the 0-30 cm and 30-60 cm of soil layer, respectively) and equalled 1) 7.37-7.78, 2) 7.65-7.85, 3) 7.74-7.79, 4) 7.62-7.67, 5) 7.58-7.70, 6) 7.61-7.73, 7) 7.60-7.69 (SMOLEŇ, SADY 2007). The lack of influence on soil pH by either of the tested, physiologically acid N fertilizer could have been caused by the favorable physicochemical properties of soil, particularly a relatively high soil buffer index and sorption capacity. Therefore, these characteristics of the cultivated soil could have considerably influenced the results of our quantitative analysis of elements in carrot storage roots.

Although the applied N fertilization had no significant influence on soil pH, diverse effects of its dose as well as the applied nitrogen compounds were found in relation to the content of available forms of Ca, K, Mg, S, Al, B, Ba, Ce, Co, Fe, Ga, La, Mn, Ni, Pb, Sr, Ti, Y, V, Ag, Cr, Dy, In, Li, Lu, Sc and Yb in both tested soil layers. The observed variation could have been caused by the interaction between the introduced mineral N forms ((N-NO₃, N-NH₄) as well as the nitrification inhibitor and the analysed elements (macro- and microelements, heavy metals and trace elements). In the present study, the changes in the soil content (in both soil layers 0-30 cm and 30-60 cm) of Ca, K, Mg, S, Al, B, Ba, Fe, Ga, Mn, Ni, Ti, Ag, Ce, Co, Cr, Dy, In, La, Li, Lu, Pb, Tm, Y and Yb induced by nitrogen fertilization were not reflected by the level of accumulation of these elements in carrot storage roots. However, there was an exception, namely the differentiated soil level of Sr, Sc and V (related to the application of ENTEC-26 and ammonium nitrate) corresponded with the concentration of these elements in carrot roots. It can be concluded that the content of the tested elements in carrot was more strongly related to the application of N fertilizers affecting the mineral uptake from soil than its interaction with the availability of the tested elements for plants. The fact that there was no direct relationship between the soil content and carrot root accumulation of the above elements could have resulted from the application of a relatively strong soil extractant, i.e. 1 M HCl. The mineral content of soil determined after extraction with strong extractants is usually weakly correlated with the concentration of respective elements in plant material (WESTERMAN 1990). Our previous studies (SMOLEŇ et al. 2010 a) indicated better applicability of 0.03 M acetic acid in comparison to 1 M HCl for the estimation of the relationship (expressed by correlation coefficients) between soil level of Al, B, Ba, Cd, Cr,

Cu, Li, Ni, Sr, Ti as well as Zn and its accumulation in carrot roots. The weak effect of N nutrition on the content of available forms of micronutrients and heavy metals in soil has been previously reported by CZEKAŁA and JAKUBUS (2006) (26- year field-trial study carried on medium sands) as well as ŁUKOWSKI (2006) [three-year experiment conducted on typical brown soil].

Nitrogen fertilization often strengthens the dilution effect on other nutrient elements i.e. reduced plant concentration of macro- and micronutrients as well as trace elements and heavy metals due to increased crop yield (GĘBSKI 1998, SORENSEN 1999). Nevertheless, it was also shown that more intense plant growth occurring as a result of N fertilization may enhance the uptake of heavy metals by crops (GIORDANO, MORTVEDT 1976). In the present study, the highest total yield of carrot storage roots was obtained after the application of ENTEC-26 35+35 kg N ha⁻¹ – the data shown in the earlier publication by SMOLEŃ, Sady (2008 a). The yield of carrot fertilized with ammonium nitrate in a dose of 70+70 or 105+105 kg N ha⁻¹ was lower than noted for the control plants. Thus, it can be stated that the interaction of nitrogen applied in the form of NO₃⁻ or NH₄⁺ as well as SO₄²⁻ (from ENTEC-26) with mineral elements in soil environment (Ag, Al, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, Sc, Sn, Sr, Ti, Tm, Y, Yb and V) could have remarkably modified the results obtained during our study. This statement encompasses both potentially antagonistic or synergistic effects between particular elements (during the uptake stage) as well as chemical interactions occurring in soil solution. As a result, different forms (speciations) of tested elements, characterized by various solubility and availability for plants, may have occurred in soil (UYGUR, RIMMER 2000, MARCINKONIS 2008). In the present study, the aforementioned factors could have significantly influenced the uptake of particular elements by plants and thus affected the level of their accumulation in carrot storage roots.

It is interesting to notice that fertilization with ENTEC-26 (containing sulphur in the form of S-SO₄) had no effect on S content in carrot storage roots in comparison to ammonium nitrate nutrition. Very little sulphur could have been leached by precipitation water to soil layers deeper than 60 cm, a conclusion which is confirmed by the results of soil analysis after carrot cultivation. The results can be explained by a relatively low demand of carrot for sulphur.

The fertilizers used in our experiment, i.e. ENTEC-26 and ammonium nitrate, had variable effect (depending on a nitrogen dose) on the content of Co, Fe, In, Li, Ni, Sc, Y, Yb and V in carrot roots. This variation could have been caused by adverse chemical properties, different solubility in soil (i.e. forming speciations of differential availability for plants) as well as different mobility of particular elements in the soil-plant system. Mineral transport in this system is affected, for example, by physicochemical properties of soil (TYLER, OLSSON 2001). At this point, let us cite the results of the study conducted by TILLS, ALLOWAY (1981), which suggested that nitrogen applied in

the ammonium form lowered the copper concentration in wheat grown on copper-deficient soil when compared with the nitrate source of nitrogen. Increasing concentrations of ammonium ions in solution culture reduced both plant concentration of copper as well as vegetative yield. MARSCHNER, RÖMHELD (1993) stated that accumulation of Fe, Mn, Zn, and Cu in bean plants was higher after fertilization with N-NH₄ (especially when combined with the nitrification inhibitor N-Serve) than application of N-NO₃. Total-N, P, K and Mg concentrations in flue-cured tobacco leaves were non-significantly affected by the form of nitrogen fertilizer forms: 100% N-NO₃, 100% N-NH₄, 50%+50% N-NH₄+N-NO₃ (KARAIVAZOGLU et al. 2007). In the research conducted by ZACCHEO et al. (2006), 15-day incubation of soil with (NH₄)₂SO₄+nitrification inhibitor DMPP as well as Ca(NO₃)₂ did not significantly affect soil pH when compared to strongly acidic activity of (NH₄)₂SO₄ and (NH₄)₂S₂O₃. On the other hand, application of (NH₄)₂SO₄+DMPP contributed to a significant increase in the content of Cd, Cu, Ni, Pb and Zn in sunflower shoots in comparison to fertilization with Ca(NO₃)₂. XIE et al. (2009) revealed that the acidification occurring due to treatments with N-NH₄ and N-NH₄ with the nitrification inhibitor DCD increased the concentrations of extractable Cd and Zn, both of which were largely depleted in the rhizosphere. However, the total uptake of Cd and Zn was the highest in the N-NO₃ treatment, despite the fact that concentrations of extractable Cd and Zn in the rhizosphere were the lowest in this combination.

RODRÍGUEZ-ORTÍZ et al. (2006) showed that application of NH₄NO₃ in doses of 50, 100 and 150 mg N kg⁻¹ increased Cd and Pb accumulation in tobacco plants higher than soil fertilization with CO(NH₂)₂ in 50 and 100 mg N kg⁻¹ doses. In the studies conducted by JURKOWSKA et al. (1981) as well as JURKOWSKA and ROGÓZ (1981), N fertilization (as ammonium nitrate, calcium nitrate, urea and ammonium sulphate) resulted in increased levels of macronutrients (N, P, S, Cl, K, Na, Ca and Mg) and micronutrients (Fe, Mn, Zn, Cu, Mo and B) taken up by barley and sorrel plants cultivated in a pot experiment. In the case of microelements, JURKOWSKA and ROGÓZ (1981) observed differences in the influence of the tested fertilizers on the uptake of micronutrients, which were related to the influence of these compounds on soil pH. Application of various nitrogen treatments (including ammonium sulphate, ammonium nitrate and urea) in red cabbage grown on heavy soil (pH_{H₂O} 6.89) significantly affected the levels of Al, Cu, Fe, Mn, Sr, Zn, Cd, Co, Li, Mo Ti and V in cabbage heads (SMOLEŃ, SADY 2008b). Nevertheless, the tested fertilizers did not have a statistically verifiable effect on the concentration of B, Cr, Ni, Pb and Ti in cabbage. In the research conducted by DOMAGAŁA et al. (2009) on ammonium sulphate and RSM (solution of ammonium nitrate + urea), interaction between an N dose with the method of its introduction to soil (placement and broadcast technique application) and concentration of Cd, Cr, Cu, Fe, Mn, Ni, Sr and Zn in white cabbage was dependent on the physicochemical parameters of soil, especially soil reaction

($\text{pH}_{\text{H}_2\text{O}}$ 7.18-8.21), in each year of the study. In this context, the results of our previous study (SMOLEŃ, SADY 2009c) on pot cultivation of carrot cv. Kazan F₁ fertilized with different types of N compounds: calcium and ammonium nitrate, ammonium sulphate as well as urea, seem interesting. In that experiment, among all the analyzed elements (Al, As, B, Ba, Be, Ca, Co, Cr, Fe, Ga, In, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti and V), nitrogen fertilization (irrespective of the applied compound) contributed to increased uptake of Mg and Se by carrot plants when compared to the control (cultivated without N addition). Treatment with ammonium sulphate led to reduced concentration of Ba and Mo as well as increased Mn content in carrot roots. As a result of calcium nitrate application, higher accumulation of Sr and Be in carrot was observed. In the present study, different results were found than those obtained in the previously mentioned pot experiment (SMOLEŃ, SADY 2009c) in respect of N fertilization affecting the mineral composition of storage roots of carrot cv. Kazan F₁, including the content of macro- and micronutrients, heavy metals and trace elements. Conditions of plant cultivation (field experiment), with a particular emphasis on different physicochemical properties of soil as well as application of lower nitrogen doses introduced with other fertilizers, can possibly explain such discrepancy.

Other authors (CZEKAŁA, JAKUBUS 2006, JENTSCHKE et al. 1998, KARAIVAZOGLOU et al. 2007, ŁUKOWSKI 2006, MAIER et al. 2002, MARSCHNER, RÖMHELD 1993, RODRÍGUEZ-ORTÍZ et al. 2006, SADY, ROZEK 2002, SADY et al. 1999, 2000) have rarely included in their work on agronomic factors affecting mineral nutrition the heavy metals and trace elements presented in our study. Each of these elements (Ag, Al, Ba, Ce, Co, Cr, Dy, Ga, In, La, Li, Lu, Ni, Pb, Sc, Sn, Sr, Ti, Tm, Y, Yb and V) is characterized by specific physicochemical properties and mobility in the soil-plant system (TYLER, OLSSON 2001). The deleterious effect on human and livestock health of the above elements is not very well recognized, particularly in the context of their intake (introduction to the food chain) due to excessive accumulation in consumed plants. What is better understood is the negative impact of some speciations of these elements on organisms resulting from environmental contamination (CHMIELNICKA 2002). Thus, it is exceptionally difficult to discuss our results on bioaccumulation of heavy metals and trace elements in carrot in comparison with the data provided by other authors. Those elements were relatively rarely analyzed due to limited access to high-performance analytical devices, which enable determination of chemicals appearing in very small quantities. Out of all the elements classified as heavy metals, the European regulations provide maximum permissible levels in vegetables of just two elements: Cd and Pb (*Commission Regulation...*2001). In the case of lead, the threshold is set at 100 $\mu\text{g Pb kg}^{-1}$ f.w. In the present study, the Pb content in carrot did not exceed the maximum level and remained in the range of 19.03-77.64 $\mu\text{g Pb kg}^{-1}$ d.w. (Table 4), i.e. 2.12-8.66 $\mu\text{g Pb kg}^{-1}$ f.w., which means it was tens of fold lower than the permissible level.

In conclusion, the results presented in this paper provide some basic knowledge on the content of heavy metals and trace elements in carrot storage roots as well as their availability in soil resulting from applied nitrogen fertilization. Because we lack norms on maximum permissible levels of heavy metals and trace elements in vegetables (except Cd and Pb), it is difficult to evaluate the effect of the tested nitrogen application on the biological quality of carrot yield. Our research has been carried out on soil characterized by such physicochemical properties that ensured carrot yield with a relatively low content of cadmium (SADY et al. 1999, 2000, SADY, ROŽEK 2002, SMOLEŇ, SADY 2006), which is particularly important for production of baby food. Thus, it is an interesting finding that the nitrogen fertilization tested in this experiment had no significant influence on the content of numerous, potentially toxic elements in carrot roots, including Ag, Al, Ba, Ce, Cr, Dy, Ga, La, Lu, Pb, Sn and Ti.

CONCLUSIONS

1. Nutrition with nitrogen had significantly affected the content of Co, Fe, In, Li, Mn, Ni, S, Sc, Sr, Y, Yb and V in carrot roots and this effect varied depending on the type of fertilization regime used in the experiment.

2. No significant impact of N fertilization was found in reference to the accumulation of Ag, Al, B, Ba, Ca, Ce, Cr, Dy, Ga, K, La, Lu, Mg, Na, P, Pb, Sn and Ti in carrot roots.

3. In relation to the control, application of all doses of either ENTEC-26 or ammonium nitrate resulted in decreased concentration of Mg, Al, B, Ba, Ce, Fe, Ga, La, Ni, Pb, Ti, Y, V, Cr, Dy, In, Li, Lu, Sc and Yb as well as enhanced accumulation of Ca, Sr and Ag in soil after carrot cultivation. Nonetheless, the revealed changes in the concentration of elements in soil induced by N fertilization were not reflected in the levels of elements detected in carrot storage roots.

4. Comparable doses of nitrogen introduced with ENTEC-26 and ammonium nitrate did not significantly influence soil pH or the relationship between soil and plant concentration of tested elements.

5. The results of the present experiment confirmed relatively low sulphur requirements of carrot plants.

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