THE EFFECT OF VARIOUS NITROGEN FERTILIZATION REGIMES ON THE CONCENTRATION OF THIRTY THREE ELEMENTS IN CARROT (DAucus CAROTA L.) STORAGE ROOTS

Sylwester SMOLEŃ, Włodzimierz SADY, Joanna WIERZBIŃSKA
Department of Soil Cultivation and Fertilization of Horticultural Plants
Faculty of Horticulture, University of Agriculture in Kraków
Al. 29 Listopada 54, 31-425 Krakow, Poland
Received: March 11, 2011; Accepted: June 13, 2011

Summary
Nitrogen fertilization can affect the uptake and accumulation of nutrients, heavy metals and trace elements in plants. The aim of the study was to evaluate the influence of nitrogen application on mineral composition of carrot storage roots. In 2003-2005 field experiment with carrot ‘Kazan F1’ cv. was conducted in Trzciana (50°06’ N, 21°85’ E, South-East Poland), each year on a different site within a single soil complex. The experiment was arranged in a split-plot design with four replications. The following combinations with various nitrogen fertilization regimes (presented as kg N·ha⁻¹) were distinguished: 1 - Control, 2 - Ca(NO₃)₂ 70, 3 - Ca(NO₃)₂ 70+70, 4 - (NH₄)₂SO₄ 70 and 5 - (NH₄)₂SO₄ 70+70; where 70 kg N·ha⁻¹ was used pre-sowing, whereas 70+70 kg N·ha⁻¹ was applied in two rates: pre-sowing and as top-dressing. Solid nitrogen fertilizers were added to the soil in the form of: Ca(NO₃)₂ (15.5% N) and (NH₄)₂SO₄ (21% N). In carrot storage roots as well as in soil samples collected after carrot cultivation, the content of the following elements was determined: Ag, Al, As, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, Tm, S, Sb, Sc, Sn, Sr, Ti, Y, Yb and V. Fertilization with nitrogen had significantly influenced the accumulation of Ba, Co, Dy, In, Lu, Mg, Ni, P, Pb, S, Sb, Sc, Sn and Y in carrot roots. In particular combinations, a diverse effect of N application was observed in reference to the content of mentioned elements. Revealed differences in the soil level of tested elements did not correlate (were not reflected) with the rate of its accumulation in carrot storage roots.

key words: nitrogen fertilization, heavy metals, trace elements, rare elements, mineral composition of plants

INTRODUCTION
Carrot is an economically important crop plant containing various nutrients and health-promoting compounds (Gajewski et al. 2007, Fikselová et al. 2010). In quality assessment of carrot yield (particularly intended for...
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processing purposes), accumulation in storage roots of anti-nutrient compounds negatively affecting human health, such as nitrates (Gajewski et al. 2009) and heavy metals, is also considered.

Nitrogen fertilization can affect the level of mineral nutrients (Biesiada et al. 2009, Szura et al. 2008), heavy metals and trace elements in plants (Gębski & Mercik 1997, Rodríguez-Ortíz et al. 2006) and the type of this effect depends on chemical form of nitrogen, its dose and method of application.

Among all nitrogen fertilizers, the highest acidifying and alkalizing basifying activities are respectively exerted by ammonium sulphate and calcium nitrate (Gębski 1998). Application of physiologically acid or alkaline N fertilizers can lead to increased or reduced solubility of mineral components in soil (and its availability for plants) through affecting soil pH. The mentioned relations have been confirmed in numerous studies. In the cultivation of red beet and lettuce, a significantly higher accumulation of Cd, Pb and Zn was found in plants fertilized with (NH₄)₂SO₄ or NH₄NO₃ rather than NaNO₃ (Gębski & Mercik 1997). Rodríguez-Ortíz et al. (2006) observed that application of NH₄NO₃ in: 50, 100 and 150 mg N·kg⁻¹ doses contributed to increased concentration of Cd and Pb in tobacco in a greater degree than fertilization with 50 and 100 mg N·kg⁻¹ dose of CO(NH₂)₂.

Increase or reduction in the content of mineral elements in plants results as well from antagonistic or synergistic influence of N-NO₃, N-NH₄ and N-NH₂ forms of nitrogen on mineral uptake by plants (Marschner 1995). What is more, the effect of nitrogen application on mineral nutrition of plants depends not only on its dose and form but also on the level of other elements introduced as cations or anions with a particular fertilizer.

The influence of nitrogen fertilization on soil environment and mineral composition of plants is also determined by many other factors. These are related with physico-chemical properties of soil including: soil type, texture, redox potential and the content of organic matter (Gębski 1998, Kabata-Pendias & Pendias 1999, Kabata-Pendias & Mukherjee 2007), cation exchange capacity, base saturation ratio, soil content of Ca and Mg as well as heavy metals (Sady & Rożek 2002).

In the studies conducted by Diatta and Grzebisz (2006) the type of influence exerted by different nitrogen forms [NH₄NO₃, CO(NH₂)₂, NH₄NO₃∙CaCO₃] and doses 100 and 200 kg N·ha⁻¹ on soil level of Cd, Cu, Pb and Zn (assayed in 6 mol HCl and 1 mol CH₃COONH₄) was related to buffer capacity of soil. Little effect of N fertilization on the level of plant-available forms of microelements and heavy metals in soils was found by Czekała and Jakubas (2006) as well as Łukowski (2006).

The problem of nitrogen fertilization affecting soil environment and mineral composition of plants has been relatively well documented. Still, rarely have previous studies included the effect of N application on the changes in soil level of trace elements and its uptake by plants. The importance of numerous trace elements for living organisms is yet to be revealed. Recognition of its level in plants tissues as well as factors affecting its accumu-
lation can significantly broaden the current state of knowledge.

The aim of the work was to evaluate the effect of soil nitrogen fertilization in the form of calcium nitrate and ammonium sulphate on the content of macro- and micronutrients, heavy metals and trace elements in carrot storage roots.

MATERIAL AND METHODS

Plant material and treatments

In 2003-2005 field experiment with carrot ‘Kazan F1’ cv. was conducted in Trzciana (50°06’ N, 21°85’ E, South-East Poland), each year on a different site within a single soil complex. The carrot plants were cultivated in a three-year crop rotation including sugar beets (1st year), winter wheat (2nd year) and carrot (3rd year). Carrot was 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 seeding rate of 45 seeds·m\(^{-1}\) (1 million of seeds per hectare). The seeds were sown on 28, 24 and 30 April in the subsequent years. In all experimental years soil was classified as heavy soil. In years 2004 and 2005 soil had a comparable organic matter content - respectively 2.20% and 2.26% for 2004 and 2005 (but lower than in 2003 - 3.92%). The soil pH\(_{KCl}\) in 2003, 2004 and 2005 was respectively 6.42, 7.16 and 7.35, pH\(_{H_2O}\): 7.03, 7.80 and 7.55, while base saturation ratio (V%): 90.6%, 94.9% and 96.7%.

The experiment was arranged in a split-plot design. The following combinations with diversified nitrogen fertilization were distinguished: 1 - Control, 2 - calcium nitrate [Ca(NO\(_3\)_2 70+70 kg N·ha\(^{-1}\)], 3 - calcium nitrate [Ca(NO\(_3\)_2 70+70 kg N·ha\(^{-1}\)], 4 - ammonium sulphate [(NH\(_4\)_2SO\(_4\) 70 kg N·ha\(^{-1}\)] and 5 - ammonium sulphate [(NH\(_4\)_2SO\(_4\) 70 kg N·ha\(^{-1}\)] and 70 kg N·ha\(^{-1}\) was used pre-plant, whereas 70+70 kg N·ha\(^{-1}\) nitrogen was applied pre-plant and as a top dressing, respectively. Pre-sowing nitrogen fertilization was conducted shortly before bed formation, whereas top dressing was performed at canopy closure. Solid nitrogen fertilizers were added to the soil as Ca(NO\(_3\)_2 (15.5% N) and (NH\(_4\)_2SO\(_4\) (21% N). Each experimental treatment was randomized in four replications on 2.4 m × 6 m (14.4 m\(^2\)) plots. The total area used for experiment was 288 m\(^2\).

Carrots were harvested on 15, 24 and 08 September in the subsequent years. At harvest, about 5 kg of carrot storage root samples were collected in four replications for analyses.

A detailed description of the cultivation, climatic conditions as well as results concerning yield and chemical analyses of storage roots and soil were presented in previous works (Smoleń & Sady 2006, 2008a, 2009a,b, 2011). These included, among others, yield assessment (Smoleń & Sady 2008 a), nitrogen nutrition – level of NO\(_3\)\(^-\), NH\(_4\)\(^+\), N-total as well as N-uptake by carrot storage roots (Smoleń & Sady 2009a), content of phenolic compounds, soluble sugars and carotenes (Smoleń & Sady 2009b) as well as accumulation of Cd, Cu and Zn in carrot roots and soil after carrot cultivation (Smoleń & Sady 2006). Detailed analyses of changes in pH and the concentration of mineral nitrogen, Cd, Cu, Pb and Zn in soil before and after cultivation were also presented (Smoleń & Sady 2011).
Results of above-mentioned studies were discussed in further chapters of the work.

**Plant analysis**

In each year, shredded plant material (carrot storage roots) was dried at 70°C and ground. Carrot samples were mineralized in 65% super pure HNO$_3$ (Merck no. 100443.2500) in a CEM MARS-5 Xpress microwave oven (Pasławski & Migaszewski 2006). In mineralized plant samples the concentration of Ag, Al, As, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, Tm, S, Sb, Sc, Sn, Sr, Ti, Y, Yb and V was determined using the ICP-OES technique.

**Soil analysis**

Soils samples from all years of the study were collected during carrot harvesting for each nitrogen fertilization treatment. The samples were dried in the open air, ground, sieved with 1 mm mesh sieve. Subsequently, soil extraction with 1 mol HCl was carried out according to Rinkis method (Gorlach et al. 1999). In obtained extracts the same elements as in carrot roots were determined using ICP-OES technique. Soil extraction with 1 mol HCl is commonly applied for the analysis of the micro nutrient content in soil. Previous studies (Smoleń et al. 2010) revealed the applicability of this method to assess the relation between soil content of Co, Fe, Mn, Mo and Pb and accumulation of these elements in carrot storage roots.

**Determination of the elements**

The content of thirty-three elements (Ag, Al, As, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, Tm, S, Sb, Sc, Sn, Sr, Ti, Y, Yb and V) in carrot and soil samples was determined with the use of a Prodigy Teledyne Leeman Labs USA spectrometer ICP-OES. The ICP-OES instrument was calibrated using Merck’s ICP multi-element standard no. VI and no. XVI, Inorganic Ventures ICP single element standards of Ca, K, Mg, Na, P and S as well as standard no. 69 with group of rare elements.

**Statistical analysis**

Obtained results were statistically verified by ANOVA module of Statistica 8.0 PL program for significance level $P<0.05$. Changes of any significance were assessed with the use of variance analysis. In case of significant changes homogenous groups were determined on the basis of Duncan test.

**RESULTS**

Presented results of the study indicate that diverse N fertilization with ammonium sulphate and calcium nitrate applied pre-plant in one dose (70 kg N·ha$^{-1}$) as well as pre-sowing and as top dressing (in doses of 70+70 kg N·ha$^{-1}$) had significantly influenced the content of Mg, P, S, Ba, Ni (Table 1), Co, Dy, In, Lu, Pb, Sb, Sc, Sn and Y (Table 2) in carrot roots. No significant changes in the level of Ca, K, Na, Al, B, Fe, Ga, Mn, Sr, Ti (Table 1), Ag, As, Ce, Cr, La, Li, Yb and V in carrot (Table 2) were found after application diverse forms and doses of N fertilizers.

Analysis of macronutrients revealed that higher doses of nitrogen (70+70 kg N·ha$^{-1}$) introduced in the form of calcium nitrate and ammonium sulphate contributed to a significant increase in Mg and S accumulation in carrot when compared to the
control (Table 1). In the case of P, this relation was confirmed only for carrot fertilized with a higher dose of calcium nitrate (70+70 kg N·ha\(^{-1}\)). The lowest level of Mg, P and S was found in storage roots of carrot cultivated on soil with addition of 70 kg N·ha\(^{-1}\) dose of calcium nitrate (applied pre-sowing). It is worth to notice that in spite of introducing sulphur into soil with ammonium sulphate, a significant increase in the level of this macronutrient was noted only in the combination with pre-sowing application of (NH\(_4\))\(_2\)SO\(_4\) (when compared to plants fertilized with comparable doses of calcium nitrate). The highest S content was found in carrot from combinations with 70+70 kg N·ha\(^{-1}\) dose of nitrogen applied as calcium nitrate and ammonium sulphate. In soil, however, the greatest concentration of this element was determined after introducing respectively 70+70 and 70 kg N·ha\(^{-1}\) dose of (NH\(_4\))\(_2\)SO\(_4\).

Apart from its effect on Mg, P and S accumulation, pre-sowing fertilization with calcium nitrate in a dose of 70 kg N·ha\(^{-1}\) contributed to a significant increase in the content of In, Lu, Sc and Sn in carrot roots when compared to the control plants (Table 2). Additionally, the level of mentioned elements, as well as Ni, in storage roots of carrot from this combination significantly exceeded its concentration determined in carrot fertilized with the same compound both as pre-sowing and top dressing in a total dose of 70+70 kg N·ha\(^{-1}\) (Table 1 & 2). Adverse observation was found in the case of ammonium sulphate, as carrot fertilized with 70+70 kg N·ha\(^{-1}\) contained remarkably higher level of Ni (Table 1). In and Lu, while accumulated less Sn (Table 2) than roots of plants treated with 70 kg N·ha\(^{-1}\) dose of (NH\(_4\))\(_2\)SO\(_4\). Among mentioned elements (Ni, In, Lu, Sc and Sn) nitrogen fertilization significantly influenced the soil level (after carrot cultivation) of 1 mol HCl-soluble forms only in the case of Lu and Sc (Table 3). Soil fertilized with 70+70 kg N·ha\(^{-1}\) dose of ammonium sulphate was characterized by the lowest content of lutetium.

The lowest accumulation of Ba was noted in storage roots of plants grown with the addition of 70+70 kg N·ha\(^{-1}\) dose of Ca(NO\(_3\))\(_2\) (Table 1). Carrot from this combination, as well as fertilized pre-sowing with ammonium sulphate (70 kg N·ha\(^{-1}\)), contained the highest level of Co (Table 2). In the remaining combinations, the content of Ba and Co remained at a comparable level to the control. No diversity in the concentration of these elements was observed in soil after carrot cultivation (Table 3).

In the case of antimony, soil fertilization with ammonium sulphate increased its concentration in carrot roots, though application of a higher dose (70+70 kg N·ha\(^{-1}\)) was more effective in this aspect (Table 2). No interaction was however found for soil concentration of Sb after carrot cultivation (Table 3). Fertilization with both levels of ammonium sulphate as well as introduction of a higher dose of calcium nitrate 70+70 kg N·ha\(^{-1}\) (combinations no. 3, 4 and 5) led to an increase in Dy as well as reduction in Pb content in carrot roots (Table 2). It was accompanied by a significant decrease in dysprosium concentration in soil (Table 3).
Table 1. Concentration of Ca, K, Mg, Na, P, S, Al, B, Fe, Ga, Mn, Ni, Sr and Ti in carrot storage roots depending on pre-plant and top dressing nitrogen fertilization (means for 2003-2005)

<table>
<thead>
<tr>
<th>Combinations</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.42</td>
<td>2.33</td>
<td>0.125 ab</td>
<td>0.66</td>
<td>0.42 ab</td>
<td>0.141 ab</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70 kg N·ha⁻¹</td>
<td>0.40</td>
<td>2.17</td>
<td>0.119 a</td>
<td>0.63</td>
<td>0.39 a</td>
<td>0.137 a</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70+70 kg N·ha⁻¹</td>
<td>0.45</td>
<td>2.37</td>
<td>0.151 c</td>
<td>0.70</td>
<td>0.46 b</td>
<td>0.175 c</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70 kg N·ha⁻¹</td>
<td>0.43</td>
<td>2.48</td>
<td>0.135 abc</td>
<td>0.69</td>
<td>0.45 ab</td>
<td>0.161 bc</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70+70 kg N·ha⁻¹</td>
<td>0.43</td>
<td>2.25</td>
<td>0.145 bc</td>
<td>0.74</td>
<td>0.43 ab</td>
<td>0.169 c</td>
</tr>
</tbody>
</table>

Test F for fertilization: n.s. n.s. * n.s. * n.s. (mg·kg⁻¹ d.w.)

<table>
<thead>
<tr>
<th>Combinations</th>
<th>Al</th>
<th>B</th>
<th>Ba</th>
<th>Fe</th>
<th>Ga</th>
<th>Mn</th>
<th>Ni</th>
<th>Sr</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>39.22</td>
<td>31.9</td>
<td>25.70 b</td>
<td>48.78</td>
<td>0.94</td>
<td>5.86</td>
<td>1.18 ab</td>
<td>14.30</td>
<td>2.77</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70 kg N·ha⁻¹</td>
<td>39.64</td>
<td>31.2</td>
<td>24.79 ab</td>
<td>54.63</td>
<td>0.70</td>
<td>5.69</td>
<td>2.42 b</td>
<td>13.90</td>
<td>2.78</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70+70 kg N·ha⁻¹</td>
<td>32.13</td>
<td>35.7</td>
<td>21.67 a</td>
<td>44.22</td>
<td>0.99</td>
<td>6.54</td>
<td>0.81 a</td>
<td>16.06</td>
<td>1.96</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70 kg N·ha⁻¹</td>
<td>28.23</td>
<td>31.8</td>
<td>24.55 ab</td>
<td>44.36</td>
<td>0.69</td>
<td>5.55</td>
<td>0.95 ab</td>
<td>14.46</td>
<td>1.75</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70+70 kg N·ha⁻¹</td>
<td>33.41</td>
<td>33.1</td>
<td>26.24 b</td>
<td>47.26</td>
<td>0.80</td>
<td>6.18</td>
<td>3.90 c</td>
<td>14.65</td>
<td>2.22</td>
</tr>
</tbody>
</table>

Test F for fertilization: n.s. n.s. * n.s. n.s. n.s. * n.s. n.s.

Note: Test F: * - means are significantly different, n.s. - not significant. Means followed by the same letters are not significantly different for P < 0.05
Table 2. Concentration of Ag, As, Ce, Co, Cr, Dy, In, La, Li, Lu, Pb, Sb, Sc, Sn, Tm, Y, Yb and V in carrot storage roots depending on pre-plant and top dressing nitrogen fertilization (means for 2003-2005)

<table>
<thead>
<tr>
<th>Combinations</th>
<th>Ag</th>
<th>As</th>
<th>Ce</th>
<th>Co</th>
<th>Cr</th>
<th>Dy</th>
<th>In</th>
<th>La</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.05</td>
<td>104.13</td>
<td>808.34</td>
<td>17.71a</td>
<td>134.12</td>
<td>31.85a</td>
<td>103.24a</td>
<td>131.01</td>
<td>41.02</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70 kg N·ha⁻¹</td>
<td>0.07</td>
<td>263.03</td>
<td>922.41</td>
<td>17.97a</td>
<td>140.40</td>
<td>35.21ab</td>
<td>137.16b</td>
<td>132.91</td>
<td>39.52</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70+70 kg N·ha⁻¹</td>
<td>0.06</td>
<td>134.78</td>
<td>883.54</td>
<td>94.35b</td>
<td>135.42</td>
<td>37.49abc</td>
<td>104.65a</td>
<td>126.81</td>
<td>38.26</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70 kg N·ha⁻¹</td>
<td>0.06</td>
<td>210.10</td>
<td>811.67</td>
<td>110.57b</td>
<td>146.89</td>
<td>43.38c</td>
<td>81.84a</td>
<td>121.35</td>
<td>45.42</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70+70 kg N·ha⁻¹</td>
<td>0.06</td>
<td>193.50</td>
<td>748.42</td>
<td>21.63a</td>
<td>136.68</td>
<td>40.57bc</td>
<td>140.24b</td>
<td>125.52</td>
<td>41.50</td>
</tr>
</tbody>
</table>

Test F for fertilization: n.s. n.s. n.s. * n.s. * * n.s. n.s.

<table>
<thead>
<tr>
<th>(µg·kg⁻¹·d.w.)</th>
<th>Lu</th>
<th>Pb</th>
<th>Sb</th>
<th>Sc</th>
<th>Sn</th>
<th>Tm</th>
<th>Y</th>
<th>Yb</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>1.45 b</td>
<td>284.38 c</td>
<td>98.40 ab</td>
<td>1.64 a</td>
<td>34.60 ab</td>
<td>&lt;l.d.</td>
<td>8.48 b</td>
<td>1.88</td>
<td>95.33</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70 kg N·ha⁻¹</td>
<td>2.18 c</td>
<td>232.82 bc</td>
<td>70.54 a</td>
<td>2.70 b</td>
<td>108.08 c</td>
<td>&lt;l.d.</td>
<td>9.39 b</td>
<td>2.23</td>
<td>105.40</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70+70 kg N·ha⁻¹</td>
<td>0.75 a</td>
<td>187.42 ab</td>
<td>63.93 a</td>
<td>1.12 a</td>
<td>47.48 b</td>
<td>0.74</td>
<td>5.80 a</td>
<td>2.63</td>
<td>95.07</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70 kg N·ha⁻¹</td>
<td>1.89 c</td>
<td>141.98 a</td>
<td>149.68 bc</td>
<td>0.94 a</td>
<td>39.24 b</td>
<td>0.18</td>
<td>5.39 a</td>
<td>1.72</td>
<td>74.61</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70+70 kg N·ha⁻¹</td>
<td>2.85 d</td>
<td>166.01 ab</td>
<td>203.95 c</td>
<td>1.54 a</td>
<td>9.51 a</td>
<td>0.63</td>
<td>8.20 b</td>
<td>1.48</td>
<td>97.01</td>
</tr>
</tbody>
</table>

Test F for fertilization: * * * * * * n.s. n.s.

Note: see Table 1
Table 3. Chemical composition of soil after carrot cultivation depending on pre-plant and top dressing nitrogen fertilization (means for years 2003-2005)

<table>
<thead>
<tr>
<th>Combinations</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>As</th>
<th>B</th>
<th>Ba</th>
<th>Ce</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>14312.0</td>
<td>102.3 c</td>
<td>1220.5</td>
<td>32.0</td>
<td>267.7 bc</td>
<td>26.9 a</td>
<td>1887.6</td>
<td>3.9</td>
<td>2.1 b</td>
<td>50.5</td>
<td>11.7 b</td>
<td>2.7</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70 kg N·ha⁻¹</td>
<td>13636.7</td>
<td>83.3 b</td>
<td>1146.9</td>
<td>29.4</td>
<td>258.4 ab</td>
<td>26.6 a</td>
<td>1700.5</td>
<td>3.7</td>
<td>1.9 ab</td>
<td>47.9</td>
<td>11.6 b</td>
<td>2.5</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70+70 kg N·ha⁻¹</td>
<td>13460.8</td>
<td>67.6 a</td>
<td>1042.9</td>
<td>27.6</td>
<td>262.9 ab</td>
<td>30.1 b</td>
<td>1411.3</td>
<td>3.3</td>
<td>1.6 a</td>
<td>41.2</td>
<td>11.0 a</td>
<td>2.3</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70 kg N·ha⁻¹</td>
<td>14472.7</td>
<td>76.6 ab</td>
<td>1158.6</td>
<td>29.1</td>
<td>270.3 c</td>
<td>41.2 c</td>
<td>1777.4</td>
<td>3.8</td>
<td>1.8 ab</td>
<td>48.9</td>
<td>11.1 a</td>
<td>2.5</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70+70 kg N·ha⁻¹</td>
<td>14109.7</td>
<td>74.4 ab</td>
<td>1123.5</td>
<td>29.2</td>
<td>252.3 a</td>
<td>62.3 d</td>
<td>1728.5</td>
<td>3.8</td>
<td>1.8 ab</td>
<td>48.7</td>
<td>11.1 a</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Test \( F \) for fertilization: n.s. * n.s. * n.s. * n.s. * n.s. * n.s. * n.s.

<table>
<thead>
<tr>
<th>Combinations</th>
<th>Cr</th>
<th>Fe</th>
<th>Ga</th>
<th>La</th>
<th>Li</th>
<th>Mn</th>
<th>Ni</th>
<th>Sr</th>
<th>Pb</th>
<th>Ti</th>
<th>Y</th>
<th>V</th>
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<tbody>
<tr>
<td>Control</td>
<td>1.7</td>
<td>4186.2</td>
<td>3.2</td>
<td>4.7 b</td>
<td>1.5</td>
<td>374.2</td>
<td>5.0</td>
<td>32.8</td>
<td>9.9 b</td>
<td>9.3</td>
<td>5.59 c</td>
<td>6.3</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70 kg N·ha⁻¹</td>
<td>1.6</td>
<td>3744.6</td>
<td>3.0</td>
<td>4.7 b</td>
<td>1.4</td>
<td>347.3</td>
<td>4.7</td>
<td>31.6</td>
<td>9.8 b</td>
<td>9.2</td>
<td>5.55 c</td>
<td>6.0</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70+70 kg N·ha⁻¹</td>
<td>1.4</td>
<td>3477.9</td>
<td>2.7</td>
<td>4.5 a</td>
<td>1.2</td>
<td>311.1</td>
<td>4.2</td>
<td>31.5</td>
<td>8.3 a</td>
<td>8.1</td>
<td>5.24 a</td>
<td>5.2</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70 kg N·ha⁻¹</td>
<td>1.6</td>
<td>4227.6</td>
<td>3.1</td>
<td>4.5 a</td>
<td>1.4</td>
<td>359.8</td>
<td>4.7</td>
<td>33.0</td>
<td>9.2 ab</td>
<td>9.2</td>
<td>5.29 ab</td>
<td>5.9</td>
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<tr>
<td>(NH₄)₂SO₄ 70+70 kg N·ha⁻¹</td>
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<td>3870.3</td>
<td>3.1</td>
<td>4.5 a</td>
<td>1.4</td>
<td>345.7</td>
<td>4.7</td>
<td>32.1</td>
<td>9.6 b</td>
<td>9.7</td>
<td>5.31 b</td>
<td>6.0</td>
</tr>
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</table>

Test \( F \) for fertilization: n.s. * n.s. * n.s. * n.s. * n.s. * n.s. * n.s. * n.s.

<table>
<thead>
<tr>
<th>Combinations</th>
<th>Ag</th>
<th>Dy</th>
<th>In</th>
<th>Lu</th>
<th>Sn</th>
<th>Tm</th>
<th>Yb</th>
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<tr>
<td>Control</td>
<td>63.1</td>
<td>584.3 c</td>
<td>561.9</td>
<td>127.2 d</td>
<td>233.6</td>
<td>94.5 d</td>
<td>214.6</td>
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<tr>
<td>Ca(NO₃)₂ 70 kg N·ha⁻¹</td>
<td>60.4</td>
<td>585.7 e</td>
<td>501.5</td>
<td>124.2 c</td>
<td>280.3</td>
<td>91.9 c</td>
<td>228.8</td>
</tr>
<tr>
<td>Ca(NO₃)₂ 70+70 kg N·ha⁻¹</td>
<td>64.8</td>
<td>515.5 a</td>
<td>485.3</td>
<td>122.4 b</td>
<td>210.6</td>
<td>90.7 b</td>
<td>259.5</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70 kg N·ha⁻¹</td>
<td>63.9</td>
<td>515.1 a</td>
<td>575.1</td>
<td>124.6 c</td>
<td>318.7</td>
<td>93.0 c</td>
<td>234.3</td>
</tr>
<tr>
<td>(NH₄)₂SO₄ 70+70 kg N·ha⁻¹</td>
<td>62.0</td>
<td>539.3 b</td>
<td>551.8</td>
<td>120.4 a</td>
<td>217.4</td>
<td>88.8 a</td>
<td>201.3</td>
</tr>
</tbody>
</table>

Test \( F \) for fertilization: n.s. * n.s. * n.s. * n.s. * n.s. * n.s. * n.s. * n.s.

Note: see Table 1
Application of ammonium sulphate (irrespective of its dose) as well as fertilization with 70+70 kg N·ha⁻¹ calcium nitrate (combinations no. 3, 4 and 5) increased thulium accumulation in carrot roots when compared to other tested combinations. In the control as well as due to pre-sowing introduction of 70 kg N·ha⁻¹ Ca(NO₃)₂, Tm content in carrot remained below the limits of its detection by ICP-OES spectrometer. No diversity in thulium concentration was noted in all tested soil samples (Table 3).

It should be mentioned that in spite of significant changes in K, B, Ce and La content observed in soil after plant cultivation (Table 3), no such relations were found for the level of these elements in carrot storage roots.

DISCUSSION

Each of the tested elements is characterized by diverse chemical properties and mobility within both soil as well in soil-plant system (Kabata-Pendias & Mukherjee 2007). Movement of elements in the latter system depends on numerous physico-chemical properties of soil including: pH, sorption properties, organic matter content and type of accompanying ions in soil solution (Gębski 1997, Tyler & Olsson 2001). Additionally, mobility of elements between soil and plant is influenced by physiological and biochemical processes related to mineral nutrition of plants (Marschner 1995, Kabata-Pendias & Mukherjee 2007).

Gębski (1997) as well as Gębski and Sommer (1997) revealed that sulphate ions reduced, in relation to chlorides, Cd, Cu, Pb and Al desorption in soil. Studies conducted by McLaughlin et. al. (1998) showed that Cd concentration in soil solution increased more consistently with increasing concentrations of S-SO₄ compared to N-NO₃ in soil solution. In the present work, fertilization with both doses of ammonium sulphate decreased K, Ce, La, Lu, Sc and Yb concentration in soil below the control level - after soil extraction with 1 mol HCl. Still, the obtained changes were not reflected by plant accumulation of mentioned elements. Previous studies (Smoleń et al. 2010) indicated an applicability of soil extraction with 1 mol HCl for the evaluation of relation between Co, Fe, Mn, Mo and Pb content in three layers of soil (0-30 cm, 30-60 cm and 60-90 cm) and its level in carrot storage roots. However, much stronger interactions were found in the case of: Al, B, Ba, Cr, Li, Ni, Sr, Ti and Zn extracted using 0.03 mol acetic acid (Smoleń et al. 2010). The possible explanation could be that results of chemical composition of soil obtained after extraction with strong agents usually weakly correlate with the level of mineral uptake by plants (Westerman 1990).

Studies conducted by Diatta and Grzebisz (2009) as well as Diata et al. (2009) on acid soil contaminated with heavy metals revealed that soil application of calcium (introduced with Ca fertilizers) lowered heavy metal concentration in soil solution through increasing its pH. As a consequence, it reduces its uptake by cultivated plants. Soil used in the present experiments with carrot cultivation was characterized by a relatively low content of heavy metals as well as favorable physico-chemical properties, particul-
early: soil pH, base saturation ratio and quite high content of organic matter. Nitrogen fertilizers applied in the study had no significant influence on soil pH – detailed data presented in previous works (Smoleń & Sady 2006, 2011). Average pH of soil after carrot cultivation in each combination was: 1 - 7.54, 2 - 7.60, 3 - 7.61, 4 - 7.59, 5 - 7.52. As it was previously showed by Sady et al. (1999) as well as Sady and Rożek (2002) for carrot cultivation on soils characterized by differential physico-chemical properties (including various content of heavy metals), the strongest influence on the uptake and accumulation of cadmium by plants is exerted by soil pH as well as base saturation ratio. It is worth to mention that in our studies no significant effect of fertilization with diverse N doses and forms was observed with reference to Cd and Zn content in carrot roots (data published previously (Smoleń & Sady 2006). On the other hand, application of 70+70 kg N·ha$^{-1}$ ($\text{NH}_4$)$_2\text{SO}_4$ lowered Cu level in carrot in comparison to other combinations of the study (Smoleń & Sady 2006).

Nitrogen fertilization is often accompanied by a dilution effect i.e. reduction in percentage content of mineral nutrients in plants due to increased yield (Gębski 1998, Sorensen 1999). In our studies, however, N fertilization did not influence carrot yield (detailed data published previously (Smoleń & Sady 2008). In such a case, it can be assumed that revealed changes in Mg, P, S, Ba, Ni, Co, Dy, In, Lu, Pb, Sb, Sc, Sn and Y content in carrot roots were induced by interrelations between various forms of nitrogen ($\text{NO}_3^-$, $\text{NH}_4^+$), accompanying ions ($\text{Ca}^{2+}$, $\text{SO}_4^{2-}$) and mineral elements occurring in soil environment. What should be taken into consideration is a potentially antagonistic or synergistic action of particular elements on mineral uptake by plants as well as its interrelations leading to formation of various speciations in soil. The latter ones can be characterized by adverse solubility in soil solution as well as availability for plants (Uygur & Rimmer 2000, Kabata-Pendias & Mukherjee 2007, Marcinkonis 2008). The above-mentioned factors could have significantly affected the uptake of particular mineral elements by carrot and consequently the level of its accumulation in storage roots.

Obtained results showed that introduction of Ca (applied with calcium nitrate) did not increase its content in carrot when compared with other tested combinations. This observation can be linked to a relatively high, natural level of calcium in soil. Similarly, additional supply of sulphur after soil application of ammonium sulphate did not clearly contributed to increase content of this element in carrot storage roots with the exception pre-sowing fertilization with ammonium sulphate compared with pre-sowing application of calcium nitrate. It can indicate that the natural level of sulphur in soil completely fulfilled carrot needs. Mineral nutrient requirements of carrot towards sulphur are relatively small, what can explain the lack of increase in its uptake by carrot after top-dressing fertilization with ammonium sulphate.

Interesting is to compare our results with those obtained by other authors, especially in the aspect of
macro and microelement content (Ca, K, Mg, Na, P, S, B, Fe, Mn) in carrot. In the present study, basically no influence of N application was revealed on the plant accumulation of mineral elements from this group (except for Mg, P and S). In the studies conducted by Jurkowska et al. (1981) as well as Jurkowska and Rogóź (1981), soil fertilization with nitrogen, in the form of ammonium nitrate, calcium nitrate, urea and ammonium sulphate, contributed to an increased uptake of: N, P, S, Cl, K, Na, Ca, Mg, Fe, Mn, Zn, Cu, Mo and B by barley and sorrel plants cultivated in a pot experiment. Revealed changes in the effect exerted by particular fertilizer on microelement uptake by plants were dependent on its influence on soil pH (Jurkowska & Rogóź 1981). Results obtained by Sorensen (1999) indicated that soil fertilization with calcium nitrate in a dose of: 0, 60, 120 and 240 kg N·ha$^{-1}$ reduced P, K, B, and Fe (a dilution effect) as well as increased Ca, Na and Mn content in carrot storage roots. Application of four different nitrogen fertilizers (calcium nitrate, ammonium sulphate, ammonium nitrate and urea) in red cabbage cultivation on heavy soil (pH$_{H_2O}$ 6.89) significantly influenced the level of Al, Cu, Fe, Mn, Sr, Zn, Cd, Co, Li, Mo Ti and V in cabbage heads (Smoleń & Sady 2008b). These tested fertilizers did not however significantly affect B, Cr, Ni, Pb and Ti concentration in cabbage. In the mentioned study, heads of cabbage plants fertilized with calcium nitrate and urea were characterized by the highest content of Al, Mn, Sr, Zn, Cd and Mo. Urea caused a significant increase in the content of Cu, Li and V, while ammonium nitrate resulted in an elevated level of Fe and Co in cabbage heads. Fertilization with ammonium sulfate led to a substantial decrease in the content of Al, Mo and V while application of ammonium nitrate caused a decline in Sr concentration in cabbage. In three-year studies conducted by Domagała-Świątkiewicz et al. (2009) the effect of a dose as well as application method (placement and broadcast technique) of ammonium sulphate and RSM (solution of ammonium nitrate + urea) was observed in respect of: Cd, Cr, Cu, Fe, Mn, Ni, Sr and Zn content in white cabbage heads. This interaction was strongly related to physico-chemical properties of soil - especially soil pH ranging in particular years of the experiment from 7.18 to 8.21 (pH$_{H_2O}$). Basing on presented results it can be stated that the influence of various forms of N fertilizers on the uptake and accumulation of mineral nutrients depends not only on soil factors but also on cultivated plant species.

It is worth to mention that among Ni, In, Lu, Sc and Sn (mineral elements with differentiated content in carrot roots tested in the experiment), nitrogen application significantly diversified the soil content of 1 mol HCl soluble forms only in the case of Lu and Sc. The lowest level of Lu detected in soil fertilized pre-sowing and as a top-dressing with ammonium sulphate could be related to its increased uptake by plants. This consequently contributed to the highest noted accumulation of lutetium in carrot roots from that combination. Revealed diversity in Sc content in carrot roots was not reflected by its
level in soil after carrot cultivation. With a comparable content of Tm in soil, 70+70 kg N·ha\(^{-1}\) dose of nitrogen applied in the form of calcium nitrate and ammonium sulphate (as well as lower dose of \((\text{NH}_4)_2\text{SO}_4\) - to the lesser extent) contributed to an increased concentration of thulium in carrot. Thus, obtained results indicate that higher concentrations of N as well as top-dressing fertilization with nitrogen (irrespective of its form) can improve the uptake and accumulation of thulium.

Interesting is the revealed influence of tested nitrogen fertilizers on the content of Dy, Pb and Sb in carrot roots. Application of ammonium sulphate in both doses significantly increased Sb and Dy level in carrot. High content of Dy in carrot from combinations no. 4 and 5 (higher dose of calcium nitrate as well as both doses of ammonium sulphate) can indicate improved uptake of this element from soil. In these three combinations reduced soil concentration of easily soluble forms of dysprosium was noted. Striking is the observation of decreased level of Pb in carrot roots fertilized with ammonium sulphate as a significantly lower concentration of lead was found only in soil treated with 70+70 kg N·ha\(^{-1}\) dose of calcium nitrate (when compared to the control). Application of ammonium sulphate (physiologically acid N fertilizer) reduced Pb content in carrot more effectively than introduction of physiologically alkaline calcium nitrate. It can be related to high values of: soil pH, base saturation ratio and elevated content of Ca and Mg in soil. These particular soil properties are proved to reduce the accumulation of heavy metals in plants (Gębski 1998, Sady & Rożek 2002).

Taking into consideration all the results obtained in the study, it is worth to mention the previous pot experiments with carrot ‘Kazan F\(_1\)’ fertilized with various forms of N: calcium nitrate, ammonium nitrate, ammonium sulphate and urea (Smoleń & Sady 2009c). In that study, among all tested mineral 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 application (irrespective of its form) contributed to higher Mg and Se accumulation in carrot when compared to the control. Introduction of ammonium sulphate significantly reduced Ba and Mo as well as increased Mn content, while fertilization with calcium nitrate resulted in higher level of Sr and Be in carrot storage roots. In the present study, a somewhat adverse effect of applied forms and dose of N fertilizers was noted in relation to accumulation of mentioned elements in carrot, with a particular attention on Mg, Ba, Mn and Sr. A possible explanation for obtained differences can be found in different agronomic conditions of carrot growing in respect of: type of cultivation system (field and pot), physicochemical properties of soil as well as climatic conditions throughout experiments.

CONCLUSIONS

The presented study basically showed that nitrogen fertilizers only slightly influenced chemical properties of soil (mainly pH), solubility rate of mineral nutrients in soil environment and, thus, mineral uptake (and
accumulation) by carrot plants. Such an observation can result from a relatively high buffer capacity of tested soil. With the lack of effect exerted by tested mineral fertilizers on soil pH, obtained changes in Mg, P, S, Ba, Ni, Co, Dy, In, Lu, Pb, Sb, Sc, Sn and Y content in carrot roots were mainly determined by interactions (antagonistic or synergistic) between these elements and nutrients introduced with N compounds: NH$_4^+$, NO$_3^-$ as well as Ca$^{2+}$ and SO$_4^{2-}$. Revealed differences in the concentration of 1 mol HCl - soluble forms of mineral elements in soil generally were not reflected with its level in carrot. It can be, therefore, stated that mentioned interactions between compounds applied to soil and: Mg, P, S, Ba, Ni, Co, Dy, In, Lu, Pb, Sb, Sc, Sn and Y took place either at the uptake level or within the rhizosphere. Lack of the relation between observed diversity in soil content of tested elements and its accumulation in carrot roots could have resulted from using too strong solution for soil extraction - 1 mol HCl. Using this particular extractant allows to determine both soluble and potentially available forms for plants - exchangeable forms bound in the sorption complex and weakly soluble salts (speciations). Most probably, application of a milder agent (e.g. 0.03 mol acetic acid) or sequential extraction procedure would have allowed to determine content of mineral elements in soil at a different level but correlating better with its accumulation in carrot storage roots.

Acknowledgements
The present studies with carrot cultivation were financed by Alima-Gerber Enterprise (in 2003-2004) as well as the Polish Ministry of Science and Higher Education - project No. 2 P06R 022 28, implemented in 2005-2006.

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Wpływ zróżnicowanego nawożenia azotem na zawartość trzydziestu trzech pierwiastków w korzeniach spichrzowych marchwi (*Daucus carota* L.)

**Streszczenie**

Nawożenie azotem może wpływać na pobieranie i akumulację składników pokarmowych, metali ciężkich i pierwiastków śladowych przez rośliny. Celem badań była kompleksowa ocena wpływu nawożenia azotem na skład mineralny korzeni spichrzowych marchwi. Trzyletnie badania z uprawą marchwi ‘Kazan F1’ cv. przeprowadzono w miejscowości Trzciana (50°06’ N, 21°85’ E). Doświadczenie założono metodą split-plot w czterech powtórzeniach. W badaniach zastosowano kombinacje ze zróżnicowanym nawożeniem azotem (w kg N∙ha⁻¹): 1 - Kontrola, 2 - Ca(NO₃)₂ 70, 3 - Ca(NO₃)₂ 70+70, 4 - (NH₄)₂SO₄ 70 i 5 - (NH₄)₂SO₄ 70+70, gdzie 70 kg N∙ha⁻¹ zastosowano przedsiennie, podczas gdy 70+70 kg N∙ha⁻¹ aplikowano przedsiennie i pogłównie. Azot zastosowano w formie nawozów azotowych Ca(NO₃)₂ (15,5% N) i (NH₄)₂SO₄ (21% N). W korzeniach spichrzowych oraz w glebie po uprawie marchwi oznaczono zawartość: Ag, Al, As, B, Ba, Ca, Ce, Co, Cr, Dy, Fe, Ga, In, K, La, Li, Lu, Mg, Mn, Na, Ni, P, Pb, Tm, S, Sb, Sc, Sn, Sr, Ti, Y, Yb i V przy zastosowaniu techniki ICP-OES. Nawożenie azotem miało istotny wpływ na zawartość Ba, Co, Dy, In, Lu, Mg, Ni, P, Pb, S, Sb, Sc, Sn i Y w marchwi. W poszczególnych kombinacjach stwierdzono odmienny wpływ oddziaływania nawożenia azotem na zawartość oznaczanych pierwiastków w marchwi. Wykazane różnice zawartości składników w glebie zasadniczo nie miały związku z poziomem akumulacji badanych pierwiastków w marchwi.