Optimization of macroelement contents in raspberry leaves by liming in an extremely acid soil

B. Sikiric1*, D. Cakmak1, E. Saljnikov1, V. Mrvic1, M. Jakovljevic2, O. Stajkovic1 and D. Bogdanovic3

1 Institute of Soil Science. Teodora Drajzera, 7. 11000 Belgrade. Serbia
2 Faculty of Agriculture. Nemanjina, 6. 11080 Belgrade. Serbia
3 Faculty of Agriculture. Trg Dositeja Obradovica, 8. 21000 Novi Sad. Serbia

Abstract

Raspberries thrive best in an acid soil. However, if the soil pH is lower than 5.6, lime application is necessary. In this study the effects of lime and dolomite application in combination with NPK 15:15:15 fertilizer (600 kg ha−1) on the macroelement contents (N, P, K, Ca, and Mg) in an extremely acid soil (pH 4.35) and raspberry leaves were evaluated during a three-year period. Optimal pH value for raspberry cultivation (5.84) was achieved with the application of 9 t ha−1 of lime. The mineral nitrogen (NH4+NO3)-N content and P content in the soil after liming increased significantly, but P concentration stayed below the optimal values. Additionally, no changes were noted in K concentration in the soil. The Ca concentration increased significantly in all treatments, while the Mg content increased significantly only in the treatment with dolomite. The N content in the raspberry leaves increased, but K content decreased after liming. There was no change in P content in the leaves affected by liming. Lime increased Ca content in the leaves above the optimal values, while it did not affect the initially optimal Mg content in the leaves. After liming and NPK fertilization, the concentrations of N, P and K in the leaves were still below the optimal values, indicating a need for the combination of higher rates of fertilizer with lime in raspberry cultivation in very acid soils.

Additional key words: amelioration of acid soils; macronutrient concentration; raspberry cultivation; Rubus idaeus L.

Additional key words

Resumen

Optimización del contenido en macroelementos en hojas de frambueso mediante encalado en suelos muy ácidos

Los frambuesos crecen mejor en suelos ácidos. Sin embargo, si el pH del suelo es inferior a 5,6, es necesario aplicar cal. En este estudio se evaluaron durante un período de tres años los efectos de aplicar cal y dolomita, en combinación con fertilizantes NPK 15:15:15 (600 kg ha−1), en el contenido de macroelementos (N, P, K, Ca y Mg) en un suelo extremadamente ácido (pH 4,35) y en hojas de frambueso. El pH óptimo para el cultivo del frambueso (5,84) se logró con la aplicación de 9 t ha−1 de cal. En el caso del suelo, después del encalado el contenido en nitrógeno mineral (NH4+NO3)-N y de P aumentó significativamente, pero la concentración de P se mantuvo por debajo de los valores óptimos; además, no se observaron cambios en la concentración de K; la concentración de Ca aumentó significativamente en todos los tratamientos, pero el contenido de Mg aumentó significativamente sólo en el tratamiento con dolomita. En las hojas de frambueso, después del encalado el contenido de N aumentó, pero el contenido de K disminuyó; no hubo cambios en el contenido de P; el contenido de Ca aumentó por encima de los valores óptimos, mientras que no se afectó el contenido inicial óptimo de Mg. Después del encalado y la fertilización NPK, las concentraciones de N, P y K en las hojas estaban todavía por debajo de los valores óptimos, lo que indica la necesidad de combinar mayores tasas de abono con cal en el cultivo de frambueso en suelos muy ácidos.

Palabras clave adicionales: concentración de macronutrientes; cultivo de frambuesa; mejora de suelos ácidos; Rubus idaeus.

* Corresponding author: biljana-s@sbb.rs
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Introduction

Commercial raspberry (Rubus idaeus L.) production in Serbia has increased significantly in the last decade, and the country is at the top of the world’s commercial raspberry production at the moment.

The largest raspberry plantations in Serbia have been established on extremely acid soil. Acid soils take up around one third of the soil worldwide, while in Serbia, around 60% of arable land is of acid reaction, and 30% of extremely acid. The nutrition of raspberry in extremely acid soil with the aim of gaining a high, stable yield and a high quality crop has become a particularly important topic of research in Serbia, especially after a serious problem of raspberry plantation drying up in such soil. Besides the pathogenic causes, it is believed that soil conditions (firstly, a low pH) can be a considerable reason for raspberry drying up (Stevanovic et al., 2004).

Due to the disrupted water-air regime, a deficit in certain biogenic elements (N, P, Ca, Mg, B, Mo), and the increased, often toxic concentrations of Al, Mn and Fe, acid soils represent a limiting factor of the plant production (Foy, 1984; Hafner et al., 1992; Von Uexkull and Mutert, 1995; Barcelo et al., 1996). Plants cultivated in such soils, owing to the disrupted nutrition regime are usually of limited growth (Clark, 1981; Foy, 1984).

Liming is a necessary ameliorative practice in the process of fertility increase of acid soils (Grewal and Williams, 2003; Dugalic et al., 2006). The application of lime caused the decrease of Al and Mn toxic concentrations, as well as the decrease of extremely high Fe concentrations in the soil and raspberry leaves (Sikiric et al., 2009).

However, the addition of greater amounts of Ca or Mg via liming, besides the before-mentioned advantages, can also result in the lack of certain micronutrients (Fageria et al., 1991, 1995; Mengel, 1994). Furthermore, the antagonism between the ions has a great practical significance, both in terms of their accessibility in the soil and their uptake (Ca/NH₄, K, Mg; Mg/NH₄, K, Ca) (Jakobsen et al., 1993a,b; Kastori et al., 1996). Therefore, it is of great significance to explore how the lime application affects macroelement contents in the soil and plant leaves. The appearance of symptoms of deficiency or excess of certain elements in plants varies with different plant types and species (Helyar, 1981; Kastori et al., 1996), so it is essential to conduct this type of research with raspberry, too.

The object of this study was to ascertain the influence of different lime doses and fertilization on macroelement contents (N, P, K, Ca, and Mg) in raspberry leaves, grown in extremely acid soil. The data obtained would indicate a need for appropriate fertilization in combination with liming for the optimal nutrition of raspberry, cultivated in very acid soils.

Material and methods

In order to set up a vegetation experiment with raspberry, surface soil layer (30 cm) of an extremely acid soil (Dystric Cambisol; FAO, 1998) was used. Each pot was filled with 5 kg of air-dried soil and young raspberry seedlings of Wilamet variety were planted (one per plot). The experiment was observed for three years, with constant moisture maintenance on five fertilization treatments with three repetitions. The experiment included the treatments with 3, 6 and 9 t ha⁻¹ of lime and 3 t ha⁻¹ of dolomite. «Njival Ca» with 98.5% of CaCO₃ was used in lime treatments, while «Njival Ca + Mg» with 97% of CaCO₃ and MgCO₃ in 1:1 ratio, was used as dolomite treatment (both Njival Ca and Njival Ca + Mg are products of Serbian Glass Factory, Paracin). In early spring, 600 kg ha⁻¹ NPK (15:15:15) was added to each treatment of the experiment including the control. Soil samples for analysis and plant material samples (leaves) were taken at the end of vegetation, since previous leaf samplings from the seedlings did not provide a sufficient quantity of plant material for the analyses.

Soil pH was determined with a glass electrode pH meter in 1N KCl and in H₂O (in ratio soil:KCl or H₂O 1:2.5). Available nitrogen forms in the soil (NH₄⁺, NO₃⁻) were determined by steam distillation method described by Bremner (1965). Available P and K in soil were determined by the AL-method of Egner-Riehm (Riehm, 1958), where 0.1 N ammonium lactate (pH = 3.7) was used as an extract. After the extraction, K was determined by flame emission photometry and P by spectrophotometry, after colour development with ammonium molybdate and SnCl₂ (Riehm, 1958). Soil Ca and Mg were extracted by ammonium acetate and determined with a SensAA Dual atomic adsorption spectrophotometer (GBC Scientific Equipment Pty Ltd, Victoria, Australia; Wright and Stuczynski, 1996). Soil organic C was measured with a elemental CNS analyzer, Vario model EL III (Elementar Analysensysteme GmbH, Hanau, Germany; Nelson and Sommers, 1996).
For the determination of the plant K, P, Mg and Ca leaves were burned to ash at 550°C in a muffle furnace and acid digestion with HCl was performed according to Chapman and Pratt (1961).

Phosphorus was measured by the colorimetric ammonium vanadate method and K by flame photometry (Riehm, 1958). Ca and Mg in plant samples were determined by atomic absorption spectroscopy after Chapman and Pratt (1961). Total plant N was determined with elemental CNS analyzer, Vario model EL III.

Granulometric composition of the soils was determined according to Gee and Bauder (1986).

The effect of the treatments was evaluated using analysis of variance (SPSS 16.0 program, 2007) followed by LSD test \( (p \leq 0.05) \). Correlation analysis among various parameters of soil and leaves was also conducted.

**Results**

**Lime-induced changes in soil pH and macroelement contents**

Before the experiment was set up, the soil was characterised by an extremely acid reaction (pH in H\(_2\)O and KCl was 4.35 and 3.70, respectively) and high mineral nitrogen content (NH\(_4^+\)NO\(_3^−\) 40.78 mg kg\(^{-1}\)), where NH\(_4^+\) concentration was significantly lower (30.16 mg kg\(^{-1}\)) than NO\(_3^−\) concentration (10.62 mg kg\(^{-1}\)). The content of available P and K was very low (1.48 and 7.64 mg 100 g\(^{-1}\), respectively) (Dzamic and Stevanovic, 2000) while the soil was moderately supplied with available Mg (22.1 mg 100 g\(^{-1}\)). The concentration of available Ca was near the critical value for Ca deficiency (119 mg 100 g\(^{-1}\)), but Ca:Mg ratio was optimal (3.3:1).

According to soil texture, the soil used belonged to clay-loam soils (FAO, 2006). The content of particular fractions in the soil was: coarse sand (> 0.2 mm) 2.0%, fine sand (0.2-0.02 mm) 27.2%, silt (0.02-0.002 mm) 36.8%, clay (< 0.002%) 34.0% and silt + clay fraction (< 0.02 mm) 70.8%.

Generally, a slight variation of the analysed variables was observed among the years of the experiment (data not shown). The greatest variation was observed in NH\(_4^+\) and NO\(_3^−\) content.

During the three years, in the control treatment the pH did not change significantly after NPK application and the average pH value (in H\(_2\)O) was 4.38 (Table 1). The application of all rates of lime and dolomite caused a statistically significant increase in pH in all three years of the experiment. The greatest increase in pH was in the treatment with 9 t ha\(^{-1}\) lime (average pH was 5.84), which is 1.46 pH units more than in the control treatment. The lowest pH increase was found in the treatments with 3 t ha\(^{-1}\) of dolomite and 3 t ha\(^{-1}\) of lime (in average 0.45 and 0.39, respectively). There were statistically significant differences in pH among all lime treatments.

The application of both lime and dolomite did not influence significantly organic C content in the soil in all three years of the experiment.

The NH\(_4^+\) concentration in the control ranged between 15.6 mg kg\(^{-1}\) in the first year, to 20.7 mg kg\(^{-1}\) in the second year. The application of 6 and 9 t ha\(^{-1}\) of lime resulted in a statistically significant increase of NH\(_4^+\) in all three years (Table 1). The highest NH\(_4^+\) concentration in all three years was in the treatment with 9 t ha\(^{-1}\) of lime (on average 70.5 mg kg\(^{-1}\)) (Table 1), while the least concentrations were observed in the treatments with 3 t ha\(^{-1}\) of dolomite (on average 24.4 mg kg\(^{-1}\)) and 3 t ha\(^{-1}\) of lime (on average 28.4 mg kg\(^{-1}\)). There was a positive significant correlation among pH values and NH\(_4^+\) content in the soil \( (r = 0.854) \).

In the first year of the research, there was no increase in NO\(_3^−\) and only a slight variation of NO\(_3^−\) between the treatments was observed (9.2-12.8 mg kg\(^{-1}\)), without statistical significance. On the other hand, in the second and third year, a statistically significant increase of NO\(_3^−\) in all treatments in relation to the control was observed. The highest NO\(_3^−\) concentrations were measured in the second year, and ranged from 31.2 mg kg\(^{-1}\) (in the control) to 80.5 mg kg\(^{-1}\) (9 t ha\(^{-1}\) of lime).

The available P content in the control soil did not increase after NPK fertilizer application. The application of lime influenced statistically significant increase of the available P content, in relation to the control however, the P-content was still low for raspberry cultivation. With the increase of lime dose, a minor tendency of P concentration’s increase was noted, where statistically significant variations were observed only in the third year. The highest P content was observed in the treatment with 9 t ha\(^{-1}\) of lime, in all three years (5.2 mg 100 g\(^{-1}\) on average), while the lowest in treatment with 3 t ha\(^{-1}\) of dolomite (4.1 mg 100 g\(^{-1}\) on average). A positive significant correlation among pH and available P content in the soil was determined \( (r = 0.897) \).

The content of the available K in the control soil increased after NPK fertilizer application and belonged to the class of middle potassium soil supply. The appli-
cation of lime, as well as dolomite did not lead to significant changes in K content in all three years, in relation to the control. A significant negative correlation between pH and available K content in the soil was determined only in the third year ($r=–0.754$).

In the control treatment, the average concentration of available Ca (109 mg 100 g⁻¹) belonged to the level of mid content, but still very close to the deficit limit. The application of lime, depending on the rates, as well as the application of dolomite, had a significant influence on the increase of Ca content in the soil. The highest average Ca content, as expected, was found in the treatment with 9 t ha⁻¹ of lime (205 mg 100 g⁻¹), and the smallest average content was found in the treatment with 3 t ha⁻¹ of dolomite (135 mg 100 g⁻¹). Between the treatments with 3 t ha⁻¹ of lime and 3 t ha⁻¹ of dolomite, the differences in calcium content were significant only in the first year, due to the slower dolomite solubility. A high, significant correlation between pH and available Ca content in the soil was determined ($r=0.947$), as well as negative correlation between Ca and K content in the first and second year ($r=–0.568$).

In the control treatment, a medium level of available Mg content in the soil was established (20.03 mg 100 g⁻¹ on average). With the increase of the applied lime dose there was no increase of available Mg content in the soil, in relation to the control. The application of dolomite (3 t ha⁻¹), as expected, in all three years showed significant influence on the increase of available Mg content in the soil. Average Mg content in this treat-

| Treatments                      | pH H₂O | pH KCl | NH₄ | NO₃ | NH₄ + NO₃ | P    | K    | Ca   | Mg   | C % |
|---------------------------------|--------|--------|-----|-----|-----------|------|------|------|------|-----|
| **First year**                  |        |        |     |     |           |      |      |      |      |     |
| 600 kg ha⁻¹ NPK                 | 4.40d  | 3.75d  | 15.6c| 10.2a| 25.8      | 1.53c| 15.11a| 111d | 21.9b| 1.88a|
| 3 t ha⁻¹ CaCO₃ + NPK            | 4.85c  | 4.25c  | 32.2b| 10.5a| 42.7      | 2.01ab| 13.61a| 163b | 24.9b| 1.84a|
| 6 t ha⁻¹ CaCO₃ + NPK            | 5.30b  | 4.60b  | 34.9b| 9.2a | 44.1      | 2.01ab| 14.86a| 177b | 22.8b| 1.83a|
| 9 t ha⁻¹ CaCO₃ + NPK            | 5.95a  | 5.34a  | 63.0a| 11.2a| 74.1      | 2.18a| 13.53a| 200a | 22.3b| 1.82a|
| 3 t ha⁻¹ CaMgCO₃ + NPK          | 4.90c  | 4.22c  | 20.0c| 12.8a| 32.8      | 1.70bc| 15.52a| 133c | 33.3a| 1.83a|
| LSD (0.05)                      | 0.17   | 0.25   | 5.89 | 4.33 |           | 0.25 | 2.77 | 18.9 | 4.05 | 0.12 |
| **Second year**                 |        |        |     |     |           |      |      |      |      |     |
| 600 kg ha⁻¹ NPK                 | 4.35d  | 3.80d  | 20.7c| 31.2a| 51.9      | 1.53c| 14.53a| 106d | 19.8b| 1.80a|
| 3 t ha⁻¹ CaCO₃ + NPK            | 4.75c  | 4.20c  | 27.3c| 66.5b| 93.8      | 1.87bc| 13.11a| 139c | 27.7b| 1.80a|
| 6 t ha⁻¹ CaCO₃ + NPK            | 5.25b  | 4.60b  | 64.4b| 62.3b| 126.7     | 2.09ab| 14.03a| 170b | 20.3b| 1.78a|
| 9 t ha⁻¹ CaCO₃ + NPK            | 5.74a  | 5.12a  | 93.4a| 80.5a| 173.9     | 2.22a| 13.03a| 204a | 20.9b| 1.77a|
| 3 t ha⁻¹ CaMgCO₃ + NPK          | 4.80c  | 4.10c  | 23.5c| 78.2a| 101.7     | 1.79bc| 14.61a| 138c | 30.8a| 1.78a|
| LSD (0.05)                      | 0.13   | 0.17   | 6.91 | 5.93 |           | 0.29 | 3.12 | 10.1 | 3.15 | 0.16 |
| **Third year**                  |        |        |     |     |           |      |      |      |      |     |
| 600 kg ha⁻¹ NPK                 | 4.38d  | 3.73d  | 18.2c| 26.3a| 44.5      | 1.40d| 13.28a| 109d | 18.4b| 1.79a|
| 3 t ha⁻¹ CaCO₃ + NPK            | 4.70c  | 4.11c  | 25.6b| 37.1a| 62.7      | 1.96bc| 12.04a| 137c | 21.5b| 1.78a|
| 6 t ha⁻¹ CaCO₃ + NPK            | 5.30b  | 4.63b  | 50.3a| 44.5a| 94.8      | 2.14b| 12.45a| 150b | 20.4b| 1.75a|
| 9 t ha⁻¹ CaCO₃ + NPK            | 5.82a  | 5.25a  | 55.0a| 52.8a| 107.8     | 2.40a| 11.87a| 185a | 21.0b| 1.74a|
| 3 t ha⁻¹ CaMgCO₃ + NPK          | 4.80c  | 4.19c  | 29.8b| 40.3bc| 70.1     | 1.87c| 12.70a| 133c | 28.6a| 1.74a|
| LSD (0.05)                      | 0.25   | 0.27   | 4.70 | 4.98 |           | 0.10 | 2.55 | 13.0 | 3.5  | 0.21 |
| **Mean for 3 years**            |        |        |     |     |           |      |      |      |      |     |
| 600 kg ha⁻¹ NPK                 | 4.38   | 3.76   | 18.2 | 22.6 | 40.8      | 1.48 | 14.28a| 109  | 20.03| 1.80 |
| 3 t ha⁻¹ CaCO₃ + NPK            | 4.77   | 4.19   | 28.4 | 38.0 | 66.4      | 1.96 | 12.95a| 146  | 23.03| 1.80 |
| 6 t ha⁻¹ CaCO₃ + NPK            | 5.28   | 4.61   | 36.1 | 38.7 | 74.8      | 2.09 | 13.78a| 159  | 21.17| 1.79 |
| 9 t ha⁻¹ CaCO₃ + NPK            | 5.84   | 5.24   | 70.5 | 48.2 | 118.7     | 2.27 | 12.78a| 196  | 21.37| 1.78 |
| 3 t ha⁻¹ CaMgCO₃ + NPK          | 4.83   | 4.17   | 24.4 | 39.5 | 63.9      | 1.79 | 14.28a| 135  | 30.90| 1.78 |

Values followed by the same letter in a column are not significantly different according to LSD test ($p < 0.05$).
ment was 30.90 mg 100 g\(^{-1}\), that is, 54.5% and 38% higher when compared to the control and the treatment with 3 t ha\(^{-1}\) of lime, respectively. A significant correlation between pH and available Mg content in the soil was not found (\(r = -0.110\)).

**Lime-induced changes in macroelement contents in raspberry leaves**

Biomass production increase was noted in some treatments in respect to control, depending on the experimental year. Application of 9 t ha\(^{-1}\) of lime influenced biomass production increase positively in the first year while 6 t ha\(^{-1}\) of lime had that effect in the third year. In the second year none of the treatments with lime had considerable effect on biomass production. A significant increase in biomass production in the treatment with dolomite was noted in all three years of the experiment.

In the control, the N concentration in raspberry leaves ranged from 1.77 to 1.85% (1.81 on average) (Table 2), which is significantly lower than the optimal N concentration in raspberry leaves (2.80-3.50%), according to Bergmann (1986). A significant increase of N concentration in the leaves in relation to the control was observed in the treatment with 6 t ha\(^{-1}\) of lime in the first two years (30% on average), and with 3 t ha\(^{-1}\) of dolomite in all three years of research (24% on average). Even a significantly increased N content did not reach the optimal values in any of the treatments (Bergmann, 1986).

**Table 2. Effects of different concentrations of lime and dolomite on macroelement contents in raspberry leaves**

| Treatments               | N   | P   | K   | Ca   | Mg   | Biomass g plot\(^{-1}\) |
|--------------------------|-----|-----|-----|------|------|------------------------|
| **First year**           |     |     |     |      |      |                        |
| 600 kg ha\(^{-1}\) NPK   | 1.81\(^b\) | 0.27\(^a\) | 1.64\(^a\) | 1.45\(^b\) | 0.35\(^b\) | 6.83\(^c\)            |
| 3 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.16\(^ab\) | 0.26\(^a\) | 1.58\(^a\) | 1.90\(^a\) | 0.33\(^b\) | 8.70\(^b\)            |
| 6 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.58\(^a\) | 0.22\(^a\) | 1.51\(^a\) | 1.96\(^a\) | 0.39\(^b\) | 7.38\(^c\)            |
| 9 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.09\(^ab\) | 0.25\(^a\) | 1.34\(^ab\) | 1.99\(^a\) | 0.30\(^b\) | 10.78\(^b\)          |
| 3 t ha\(^{-1}\) CaMgCO\(_3\) + NPK | 2.45\(^a\) | 0.24\(^a\) | 1.17\(^b\) | 1.52\(^a\) | 0.59\(^a\) | 12.89\(^a\)          |
| LSD (0.05)               | 0.42 | 0.04 | 0.24 | 0.17 | 0.09 | 2.01                  |
| **Second year**          |     |     |     |      |      |                        |
| 600 kg ha\(^{-1}\) NPK   | 1.85\(^b\) | 0.27\(^a\) | 1.54\(^a\) | 1.50\(^b\) | 0.39\(^b\) | 11.15\(^b\)          |
| 3 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.02\(^ab\) | 0.28\(^a\) | 1.48\(^a\) | 1.82\(^a\) | 0.31\(^b\) | 9.87\(^b\)            |
| 6 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.17\(^a\) | 0.24\(^a\) | 1.39\(^ab\) | 1.90\(^a\) | 0.43\(^b\) | 10.76\(^b\)          |
| 9 t ha\(^{-1}\) CaCO\(_3\) + NPK | 1.96\(^ab\) | 0.27\(^a\) | 1.21\(^bc\) | 1.91\(^a\) | 0.38\(^b\) | 9.86\(^b\)            |
| 3 t ha\(^{-1}\) CaMgCO\(_3\) + NPK | 2.15\(^a\) | 0.33\(^a\) | 1.08\(^b\) | 1.48\(^b\) | 0.61\(^a\) | 14.22\(^a\)          |
| LSD (0.05)               | 0.20 | 0.07 | 0.15 | 0.15 | 0.08 | 1.38                  |
| **Third year**           |     |     |     |      |      |                        |
| 600 kg ha\(^{-1}\) NPK   | 1.77\(^c\) | 0.27\(^a\) | 1.66\(^a\) | 1.51\(^b\) | 0.30\(^b\) | 12.14\(^b\)          |
| 3 t ha\(^{-1}\) CaCO\(_3\) + NPK | 1.99\(^b\) | 0.29\(^a\) | 1.48\(^a\) | 1.51\(^b\) | 0.25\(^b\) | 13.08\(^b\)          |
| 6 t ha\(^{-1}\) CaCO\(_3\) + NPK | 1.91\(^b\) | 0.24\(^a\) | 1.39\(^b\) | 1.75\(^a\) | 0.35\(^ab\) | 16.52\(^a\)          |
| 9 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.06\(^ab\) | 0.27\(^a\) | 1.38\(^b\) | 1.85\(^a\) | 0.31\(^b\) | 13.43\(^b\)          |
| 3 t ha\(^{-1}\) CaMgCO\(_3\) + NPK | 2.20\(^a\) | 0.25\(^a\) | 1.28\(^b\) | 1.40\(^b\) | 0.53\(^a\) | 16.32\(^a\)          |
| LSD (0.05)               | 0.14 | 0.07 | 0.17 | 0.14 | 0.11 | 2.10                  |
| **Mean for three years** |     |     |     |      |      |                        |
| 600 kg ha\(^{-1}\) NPK   | 1.81 | 0.27 | 1.61 | 1.49 | 0.35 | 10.04                 |
| 3 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.01 | 0.28 | 1.51 | 1.74 | 0.30 | 10.55                 |
| 6 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.22 | 0.24 | 1.43 | 1.87 | 0.39 | 11.55                 |
| 9 t ha\(^{-1}\) CaCO\(_3\) + NPK | 2.04 | 0.27 | 1.31 | 1.92 | 0.33 | 11.36                 |
| 3 t ha\(^{-1}\) CaMgCO\(_3\) + NPK | 2.27 | 0.27 | 1.18 | 1.47 | 0.58 | 14.48                 |

Values followed by the same letter in a column are not significantly different according to LSD test (\(p < 0.05\)).
The concentration of P in the control (0.27%) was within the range of optimal values (0.2-0.5%) according to Omafra (2010), but below the optimal values (0.3-0.5%) by Bergmann (1986). Low P content in the soil draws our attention more to Bergmann’s critical values according to the regional character, established for Europe. Under the liming influence, a certain tendency of P concentration change in the leaves could not be established. The P concentration varied insignificantly and inaccurately between the treatments from 0.22% (in the first year, 6 t ha\(^{-1}\) of lime) to 0.33% (second year, 3 t ha\(^{-1}\) of dolomite).

The concentration of K in raspberry leaves in the control was 1.61% and was like P concentration, within the range of optimal values (1.0-2.0%) (Omafra, 2010), that is below the optimal values (1.80-2.50%) (Bergmann, 1986). Some treatments with lime caused a decrease in K content, but dolomite had the greatest influence on the decrease of K concentration in raspberry leaves (27% on average), which showed significant changes in relation to the control in all three years. In relation to the control, a significant decrease of K concentration in the leaves was determined in the treatments with: 9 t ha\(^{-1}\) of lime, in the second and third year (19% on average for all three years) and 6 t ha\(^{-1}\) of lime in the third year (11% on average for all three years).

The content of Ca in raspberry leaves slightly varied each year. The average Ca value in the control (1.49%) was within the range of the optimal values (0.80-1.50% and 0.80-2.50%) proposed by Bergmann (1986) and Omafra (2010), respectively. The application of 6 and 9 t ha\(^{-1}\) of lime in all three years and the application of the smallest lime dose (3 t ha\(^{-1}\)) in the first two years increased Ca concentration in the leaves significantly. In relation to the control, the average increase of this element in the leaves in the treatments with 3, 6, and 9 t ha\(^{-1}\) was 17%, 25.5% and 29% respectively. The highest Ca concentration was measured in the first year, in the treatment with the highest lime rate (1.99%), when it was above the upper limit of the optimal values (Bergmann, 1986). In the treatment with 3 t ha\(^{-1}\) of dolomite, there was no increase in Ca content in the leaves in all three years in relation to the control.

The average Mg concentration in raspberry leaves in the control (0.35%) was within the range of optimal contents (0.30-0.60%; 0.25-0.50%) (Bergmann, 1986; Omafra, 2010). The application of various lime doses did not show significant influence on the content of this element. The application of dolomite brought about a significant increase of Mg concentration in the leaves, in relation to the control (in all three years). In the treatment with dolomite, the average Mg concentration in the leaves for the three-year period was 0.58%, which is 66% more than the average concentration of this element in the control. This Mg concentration surpasses the upper limit of the optimal values according to Omafra (2010).

**Discussion**

In accordance with the previous findings (Fystro and Bakken, 2005; Caires et al., 2008; Sikiric et al., 2009), the application of lime and dolomite in a relatively short period of time increased soil pH significantly which is of great significance in view of the amelioration of acid soil. The highest lime application dose (9 t ha\(^{-1}\)) increased soil pH to 5.84, which is the optimum pH value for raspberry cultivation (pH 5.8-6.5).

The major reason for liming acid soils is to improve crop growth and yields. It is suggested that in the long run, liming will increase crop yields, organic matter returns, soil organic matter content and thus, soil aggregation (Haynes and Naidu, 1998). Lime applications are known to have short-term effects in stimulating soil biological activity whilst it is also likely that liming will have long-term effects in increasing soil organic matter content. In this study no significant differences were detected in soil organic C content between all the treatments in all three years, as a consequence of the short-term character of the experiment. We detected increased biomass production of raspberry, starting with the first year after lime application, which is due to an immediate rise in a very low soil pH. The positive effects of liming usually occur through amelioration of Al and sometimes Mn toxicity and/or alleviation of Ca deficiency (Haynes and Naidu, 1998). In addition, lime-induced positive response in dry matter yield was greater and more immediate at sites where pH was below 5.3, rather than above (Fystro and Bakken, 2005).

The concentrations of mineral nitrogen (\(\text{NH}_4^+ + \text{NO}_3^-\)) in the soil before the experiment was set up, indicate the application of N-fertilizer in the previous period, since due to the extreme soil acidity, the processes of mineralization and nitrification were considerably slowed down (Kuntze and Bartels, 1975). Liming, due to the creation of the favourable conditions for the mineralization of organic matter, conditioned the increased content of the nitrogen mineral forms.
in the soil. Therefore, the highest increase of both NH\textsubscript{4}\textsuperscript{+} and NO\textsubscript{3}\textsuperscript{−} was noted in the treatment with the highest lime rate (9 t ha\textsuperscript{−1}) (Wheeler et al., 1997). The highest values of mineral nitrogen in the soil were noted in the second year of the experiment, when the effect of liming reached full-scale. Higher concentrations of NH\textsubscript{4}\textsuperscript{+}, in relation to NO\textsubscript{3}\textsuperscript{−} (the treatments with 6 and 9 t ha\textsuperscript{−1} of lime) indicate that even after the liming, the nitrification conditions were still unfavourable.

Liming caused a slight increase in N content in the leaves, due to the influence on both N increase in the soil and its easier uptake by plants (Lyngstad, 1992; Stevens and Laughlin, 1996). Moreover, the improved N uptake is also a result of the Ca influence on the increased root activity (Bailey, 1992, 1995). At the same time, the influence of the lime dose was not observed, which is in accordance with the researches of Stevens and Laughlin (1996). Low N content in the leaves, below the optimal values, is the result of a late, autumn leaf sampling, when N concentration in the leaves and stem is the lowest, owing to its movement in the reproductive organs (Kastori et al., 1996). There was no significant correlation between the N content in the soil and leaves, which could be the result of a different plant growth, that is, «dilution effect» of this element. The increase of dry matter yield is not followed by the increase of N content in the leaves (Stevens and Laughlin, 1996), which is why it is not possible to ascertain the effect of lime dose on the increase of N in the plant.

The increase in soil pH after the liming, influenced the release of one part of bound P from Al- and Fe-phosphate, which brought about a minor increase of P concentration in the soil of all Ca treatments (Haynes, 1984; Kerschberger, 1987; Gahoonia et al., 1992; Radanovic, 1996; Dugalic et al., 2006). Low P content in the leaves after the liming is a result of its low content in the soil. Moreover, a very high to toxic Al content in the plants of these treatments could have had a significant influence on the low P content in the leaves (Sikiric et al., 2009). This very high Al content conditioned both a part of P to be bound to low solubility compounds (Brown et al., 1972; Foy, 1988), and the antagonism between Ca (high concentration in the leaves, above the optimum) and P (Demchak and Smith, 1990; Jaravan and Poldma, 2004).

Lower K content in the leaves of the control treatment, below the optimal values (despite the medium content in the soil), is a result of K decreased uptake in the low pH conditions (Murphy, 1959; Foy, 1988), while Jacobson et al. (1960) reported that if pH is lower than 4, K can even be exuded by the root in the environment. Foy (1988) stressed that high Fe, Mn and Al concentrations in acid soil influence both the imbalance of enzyme activity in the root and the imbalance of absorption and the transport of Ca, Mg, P and K.

In many previous researches, the content of available K in the soil and its uptake by the plant was not considerably affected by liming (Lutz et al., 1972; Michalk and Huang, 1992; Radanovic, 1996; Jaravan and Poldma, 2004). However, some researchers observed that after liming, the content of available K in the soil increased, especially in the soils naturally lacking nutrient cations for plant growth (which is why the number of exchange places increased, after the application of lime). Positive correlation between the contents of Ca and K in the soil can also be the result of the suppression of K\textsuperscript{+} ions by Ca\textsuperscript{2+} ions from CEC into the soil solution (Bohn et al., 2001; Troeh and Thompson, 2005).

In our study, the content of available K in the soil was not significantly affected by liming. However, in some lime treatments and especially in dolomite treatments in the leaves, a significant decrease of already low K concentration was noted, in relation to the control, which is a result of antagonistic relations, between K and Ca\textsuperscript{2+}, as well as K and Mg\textsuperscript{2+} ions in the soil (Yang et al., 1996; Mengel and Kirkby, 2001; Misson et al., 2001; Baier et al., 2006). Recently, it has been shown that liming may induce potassium deficiency due to an antagonism of Ca\textsuperscript{2+} and K in root uptake (Weis et al., 2009).

In lime treatments, a significantly increased Ca content in the soil was followed by an appropriate increase of Ca content in the leaves (Fystro and Bakken, 2005). Contrary to Ca, between pH and the content of available Mg in the soil, a significant positive correlation in the soil was not determined, since the increased application of Ca conditioned the antagonism with Mg (Michalk and Huang, 1992; Jaravan and Poldma, 2004). The highest Mg values in the soil, as well as the leaves, were measured in the treatment with the lowest lime dose, while in the treatments with higher doses of lime, the content of this element was lower.

In the treatments with dolomite, a relatively smaller Ca increase and a significantly higher Mg increase in the soil were noted (Radanovic, 1996). Due to the significantly increased Mg concentration in the leaves of this treatment, a significantly higher increase of Ca concentration was impossible, due to the antagonism between the two elements (Baier et al., 2006). A posi-
tive, highly significant correlation between the contents of Ca, that is, Mg in the soil and the leaves was determined.

In conclusion, the optimal pH for the raspberry cultivation (5.84) was obtained when 9 t ha⁻¹ of lime was applied and significant increase in biomass production was detected. However, even after the liming and NPK fertilization (600 kg ha⁻¹), the concentrations of N, P and K in the leaves stayed beneath the optimal values. The concentration of Mg in raspberry leaves was optimal in all the treatments, while the concentration of Ca was optimal in the control and dolomite treatments, and above the optimum in the lime treatments. These results indicate a need for combination of higher rates of mineral fertilizer and/or organic manure with lime application in raspberry cultivation in very acid soils. Further research is required to recognize the rates and forms of mineral and organic fertilizers for the optimal raspberry nutrition.

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