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THE INCREASED CONTENT OF MICRONUTRIENTS IN CELERY, CARROT, PARSNIP AND PARSLEY PLANTS AFTER TREATMENT WITH SODIUM NAPHTHENATE

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Summary: *Young plants of celery, parsley, parsnip and carrot, grown in nutrient solution, were treated with sodium naphthenate (10^{-7} mol dm^{-3}), applying foliar and root treatments. Both treatments affected the root content of all investigated elements present in the nutrient solution, but in a different way, depending on the plant species. An average change (increase/decrease) in the contents of investigated essential elements was about 35%. Our experiments with naphthenate showed that this treatment may enhance the efficiency of essential elements uptake and increase its content in plants without changing concentration of these elements in the nutrient solution. Especially interesting results were obtained in the case of carrot, as increased contents were observed in the elements that are usually deficient in nutrition (Fe, Zn, Mn), whereas the other remained unchanged.*

Key words: *essential elements, naphthenate, celery, carrot, parsley, parsnip.*

INTRODUCTION

Micronutrient malnutrition has become a global problem of immense proportions and rapidly growing public health problem among nearly all poor people in many developing nations, affecting about 40% of the world's population (Buyckx, 1993). This problem can be overcome by increasing the content of essential micronutrients in edible parts of plants (by applying fertilizers to the soil or to the crop, by plant breeding and/or by genetic engineering) or by food fortification with micronutrients (Reddy et al., 2001; Welch and Fraham, 2004; Mayer et al., 2008; Ahmed et al., 2008). All these approaches have some serious disadvantages; for example, the application of fertilizers with increased content of micronutrients can contaminate the soils and cause certain negative effects on the uptake of some other nutrients (Frossard et al., 2000).

Naphthenic acids represent a complex mixture of cycloalkyl and alkylcarboxylic acids that are found in raw oil and fractions obtained by its distillation. These substances in low concentrations show stimulative effects on plant growth and metabolism, but in higher concentrations, naphthenic acids and their salts produce harmful effects on plants; for example, they inhibit leaf growth, stomatal conductance and net photosynthesis in aspen (*Populus tremuloides*) seedlings (Kamaluddin and Zwiazek, 2002).

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Treatment of plants with low concentrations of naphthenate (sodium or potassium salts of naphthenic acids), especially foliar treatment, stimulates many metabolic process in different plant species (Wort, 1976) and exhibits physiological activity similar to that of plant hormones of auxin and gibberelin type (Ćirin-Novta et al., 2002).

However, little is known about the effects of naphthenate on ion uptake by plants. It is known that naphthenate influenced the uptake of phosphate (Severson and Wort, 1973) and water (Kamaluddin and Zwiazek, 2002). In our previous works we showed that naphthenic acids from the fraction of atmospheric distillation (the range of boiling temperatures 168-290°C) of the Vojvodina crude oil "Velebit" exhibited a certain activity in respect of uptake of various ions.

Presence of naphthenate reduced in average by 40 % content of total and intracellular Cd in root, stem and leaves, and alleviated the harmful effect of Cd on activity of nitrate reductase and content of photosynthetic pigments (Kevrešan et al. 2004). The presence of sodium naphthenate (0.1 µM), increased significantly contents of Mn, Fe, Zn and Ni, but decreased K and Na contents in the root of young soybean plants (Kevrešan et al., 2005).

Bearing in mind the above findings, the aim of this study was to examine the effect of low concentrations of sodium naphthenate on accumulation of some essential elements by young celery, parsley, parsnip and carrot plants, i.e. plants with edible roots and above-ground parts.

MATERIAL AND METHODS

Naphthenic acids were extracted from atmospheric gas oil fraction (distillation interval 168-290°C) of the Vojvodina crude oil "Velebit" and characterized by IR spectroscopy, GC-MS analysis and other physico-chemical methods (Ćirin-Novta *et al.*, 2003). Physico-chemical characteristics of atmospheric gas oil fraction from Vojvodina crude oil "Velebit" and of obtained naphthenic acids have been presented in the above mentioned paper Ćirin-Novta *et al.* (2003). The average molecular mass of naphthenic acids was determined to be 266, and this value was used to prepare solutions of sodium naphthenate for plant treatments. Stock solution of sodium naphthenate was prepared by neutralization of 1 mM suspension of obtained naphthenic acids with sodium hydroxide.

Seeds of carrots (*Daucus carota*, cultivar Nantes), celery (*Apium Graveolens* L., cultivar Praski), parsley (*Petroselinum hortense* Hoffm., cultivar Berlinski srednje dugi) and parsnip (*Pastinaca sativa*, cultivar Dugi beli glatki) were obtained from the Institute of Field and Vegetable Crops, Novi Sad, Serbia.

Seeds were germinated on filter paper and young plants were grown in Hoagland nutrient solution of the following composition: (mM) 2.5 $Ca(NO_3)_2$; 2.5 KNO_3; 1.0 KH_2PO_4; 1.0 $MgSO_4x7H_2O$; and (µM) 23.1 B, 4.6 Mn; 0.38 Zn; 0.16 Cu; 0.052 Mo; 8.95 Fe as Fe(II)-EDTA, ten weeks. After that they were divided into three groups: control, in which plants were continued to grow in the same solution, first test group in which plants were grown in the same medium with the addition of sodium naphthenate at a concentration of 0.1 µM (root treatment) and second test group in which the plants were grown in the same medium and foliary treated by spraying the plants with solution of sodium naphthenate (0.1 µM) every third day (foliar treatment). Nutrient solution was changed every third day. After growing plants under the given conditions for 16 days, contents of K, Ca, Mg, Fe, Mn, Zn, Cu, Ni and Na in the roots and above-ground parts were determined by flame atomic absorption spectrometry after dry ashing. Plant growth was monitored by measuring fresh and dry mass at the end of experiment. Experiments were repeated three times. Statistical analyses were conducted on treatment means using the t-test procedure of statistical package Statistica 9.1.

RESULTS

The research indicates that neither foliar nor root treatment with naphthenate influenced plant growth, that is, no significant changes in of the fresh and dry mass of root and above-ground parts was observed (data not shown).

Root treatment of celery plants with naphthenate yielded an increase in the contents of Cu (82%), Mg (29%) and Ca (30%) and a decrease in the contents of Fe (18%) and Mn (15%) in the root. In the same treatment, an increase was observed in the contents of Mg (12.5%) and K (31%), and a decrease of Fe (45%), Mn (8%) and Na (74%) in the above-ground parts of the plants.

Foliar treatment yielded a decrease in the content of Mn (15%), Zn (19%) and K (23%), and an increase only in the content of Mg (21%) in the celery root. On the other hand, this treatment resulted in decreased contents of Fe (24%), Mn (27%), Ca (22%) and Na (60%) and increased contents of Cu (98%) and K (40%) (Table I).

Table 1. Effect of sodium naphthenate on the content of particular elements in the root and above-ground part of young celery plants[a]

Element	Root			Above-ground part		
	control[b]	root treatment[c]	foliar treatment[d]	control[b]	root treatment[c]	foliar treatment[d]
Fe (mg/kg)	1119.0±47.3	920.3±67.3*	1122.0±110.1	158.83±5.91	87.80±9.22*	120.83±16.35*
Cu (mg/kg)	6.95±0.37	12.64±0.90*	6.95±0.16	3.97±1.00	4.90±1.09	7.85±1.30*
Mn (mg/kg)	635.00±25.24	541.67±49.66*	340.80±18.29*	64.10±1.08	59.17±1.17*	46.60±3.25*
Zn (mg/kg)	26.25±2.70	26.04±1.28	21.34±1.84*	19.60±1.38	20.17±1.95	17.45±1.08
Mg (%)	0.28±0.02	0.36±0.03*	0.34±0.02*	0.16±0.02	0.18±0.02*	0.15±0.02
Ca (%)	0.37±0.03	0.48±0.05*	0.35±0.03	0.32±0.016	0.31±0.005	0.25±0.026*
Na (%)	0.43±0.08	0.44±0.06	0.38±0.03	0.42±0.11	0.11±0.03*	0.17±0.04*
K (%)	8.76±0.53	7.86±0.18	6.74±0.60*	9.10±1.34	11.89±0.41*	12.76±1.37*

[a]Each value is mean ± standard deviation (n=3). Values labeled by * are significantly different from control (t-test). Values are expressed on a dry weight basis.
[b]Plants grown in the nutrient solution (control).
[c]Plants grown in the nutrient solution in the presence of 10^{-7} mol dm^{-3} sodium naphthenate (root treatment).
[d]Plants grown in the nutrient solution and treated foliary with sodium naphthenate of the same concentration (foliar treatment).

Both treatments yielded increased contents of the particular elements with no decrease observed in any of them either in the root or above-ground parts of carrot. The increase in Fe content in the root was 45% in root treatment and 20% in foliar treatment, whereas in the above-ground part the respective increases were 17.7% and 18.9%. In the root treatment, increased contents were found for Mn (69%), Zn (37.5%) and Na (50%) in the root.

As for the above-ground part, increased contents of Fe were measured in both treatments and of Cu (33%) and Zn (24%) in root treatment, whereas the foliar treatment increased contents of Cu (108%) and Zn (33%) (Table II).

Table 2. Effect of sodium naphthenate on the content of particular elements in the root and above-ground part of young carrot plants[a]

Element	Root			Above-ground part		
	control[b]	root treatment[c]	foliar treatment[d]	control[b]	root treatment[c]	foliar treatment[d]
Fe (mg/kg)	480.18±22.09	693.50±91.25*	576.54±75.58*	108.09±7.60	127.18±8.52*	127.91±9.48*
Cu (mg/kg)	4.32±2.05	6.97±2.77	5.14±0.25	4.31±0.52	5.72±0.11*	8.98±0.51*
Mn (mg/kg)	119.54±32.53	201.99±13.22*	121.67±36.91	42.60±1.63	46.07±1.24	46.46±2.65
Zn (mg/kg)	29.56±5.32	40.69±7.16*	33.15±1.23	14.91±0.57	18.52±0.47*	19.84±0.93*
Mg (%)	0.21±0.03	0.24±0.05	0.22±0.01	0.20±0.01	0.19±0.01	0.21±0.01
Ca (%)	0.33±0.02	0.37±0.12	0.37±0.03	2.88±0.51	2.71±0.32	2.12±0.54
Na (%)	0.24±0.02	0.36±0.04*	0.33±0.03*	0.12±0.03	0.11±0.04	0.08±0.02
K (%)	6.71±0.26	6.47±0.62	6.63±0.96	6.75±0.34	8.97±0.91*	6.83±0.38

[a]Each value is mean ± standard deviation (n=3). Values labeled by * are significantly different from control (t-test). Values are expressed on a dry weight basis.
[b]Plants grown in the nutrient solution (control).
[c]Plants grown in the nutrient solution in the presence of 10^{-7} mol dm^{-3} sodium naphthenate (root treatment).
[d]Plants grown in the nutrient solution and treated foliary with sodium naphthenate of the same concentration (foliar treatment).

Plants of parsnip and parsley exhibited significantly lower reactions to the treatment with naphthenate: no substantial changes of the content of any of the elements tested were observed in the above-ground parts of both plants (Tables III and IV).

As for the effect of naphthenate treatment on parsley plants it was rather similar to that observed with carrot- increased contents of only sveral elements were observed, and they were: 17% for Fe, 27% for Mn and 29% for Ca in the root treatment, whereas in the foliar treatment an increase was observed only in the Fe content (14%) (Table III).

Table 3. Effect of sodium naphthenate on the content of particular elements in the root and above-ground part of young parsnip plants[a]

Element	Root			Above-ground part		
	control[b]	root treatment[c]	foliar treatment[d]	control[b]	root treatment[c]	foliar treatment[d]
Fe (mg/kg)	609.9±37.7	491.8±44.2*	638.7±38.2	249.1±27.1	254.1±30.1	240.2±25.8
Cu (mg/kg)	4.14±1.85	4.55±1.91	4.32±2.06	4.45±1.77	5.47±1.83	6.35±2.05
Mn (mg/kg)	411.1±45.7	294.3±33.4*	339.0±32.1*	41.3±8.9	45.4±9.2	42.4±8.8
Zn (mg/kg)	29.85±6.85	29.37±7.02	32.28±5.99	12.39±3.11	10.99±2.62	10.04±2.83
Mg (%)	0.25±0.03	0.23±0.02	0.24±0.05	0.23±0.02	0.25±0.03	0.25±0.03
Ca (%)	0.53±0.02	0.55±0.03	0.56±0.02	0.93±0.04	0.87±0.03	0.85±0.07
Na (%)	0.24±0.02	0.23±0.04	0.22±0.02	0.53±0.04	0.59±0.03	0.49±0.04
K (%)	5.91±0.27	5.84±0.25	5.96±0.31	5.31±0.19	5.30±0.21	4.89±0.20

[a]Each value is mean ± standard deviation (n=3). Values labeled by * are significantly different from control (t-test). Values are expressed on a dry weight basis.
[b]Plants grown in the nutrient solution (control).
[c]Plants grown in the nutrient solution in the presence of 10^{-7} mol dm^{-3} sodium naphthenate (root treatment).
[d]Plants grown in the nutrient solution and treated foliary with sodium naphthenate of the same concentration (foliar treatment).

In the case of parsnip, a decreased content was observed only in Fe (19%) in root treatment and decreased content of Mn in root treatment (28%) and foliar treatment (17.5%) (Table IV).

Table 4. Effect of sodium naphthenate on the content of particular elements in the root and above-ground part of young celery plants[a]

Element	Root			Above-ground part		
	control[b]	root treatment[c]	foliar treatment[d]	control[b]	root treatment[c]	foliar treatment[d]
Fe (mg/kg)	653.9±31.2	764.4±33.1*	746.4±22.8*	118.7±12.1	107.5±11.8	99.0±10.2
Cu (mg/kg)	6.61±1.92	5.71±1.73	5.78±1.81	4.07±1.21	4.20±1.25	5.08±1.12
Mn (mg/kg)	346.5±33.2	438.5±34.1*	382.7±34.2	39.9±6.1	37.4±5.9	38.7±5.8
Zn (mg/kg)	37.14±5.21	39.36±6.11	33.15±5.18	13.58±2.02	12.75±2.11	12.91±2.20
Mg (%)	0.39±0.02	0.31±0.03	0.36±0.04	0.22±0.03	0.21±0.04	0.24±0.04
Ca (%)	0.49±0.03	0.63±0.04*	0.43±0.03	0.54±0.04	0.61±0.04	0.55±0.04
Na (%)	0.30±0.03	0.29±0.02	0.28±0.02	0.54±0.03	0.59±0.05	0.53±0.03
K (%)	5.51±0.25	5.38±0.26	5.30±0.32	6.56±1.88	7.27±2.04	8.03±2.10

[a]Each value is mean ± standard deviation (n=3). Values labeled by * are significantly different from control (t-test). Values are expressed on a dry weight basis.
[b]Plants grown in the nutrient solution (control).
[c]Plants grown in the nutrient solution in the presence of 10^{-7} mol dm^{-3} sodium naphthenate (root treatment).
[d]Plants grown in the nutrient solution and treated foliary with sodium naphthenate of the same concentration (foliar treatment).

DISCUSSION

It is known that plant mineral nutrition and nutrient content in plants may be affected by several factors including species, cultivar, plant age, interaction with other nutrients and environmental factors (Clarkson, 1985; Fareira et al., 1997) among them: salinity (Khorshidi et al., 2009), nutrient solution composition and growing season (Fallovo et al., 2009). Plant hormones, for example auxins and cytokinins, influence the uptake of some plant mineral elements

(Babourina et al., 1998; Arkhipova and Anokhina, 2009). The combination of hydroponics and biostimulants may increase plant mineral uptake and improve the efficiency of nutrients use (Vernieri et al., 2005).

Sodium naphthenate, representing a mixture of numerous compounds (Ćirin-Novta et al., 2002; Ćirin-Novta et al., 2003) showed a specific action, which implies from the different increase/decrease in the uptake of particular ions. Fe and Mn ions, which are most affected by naphthenate treatment, are soft cations (cations having partially filled *d*-orbitals in their outermost occupied electron shells) with the smallest ionic radius among the investigated ions. These results are in agreement with our previous findings with soybean plants (Kevrešan et al., 2005).

Humic acids, a complex mixture of aromatic organic acids present in a soil, affects plant mineral nutrition of plants and accumulation of some mineral nutrients (Verlinden et al., 2009). These substances, present at low concetrations (similar to the concentrations of sodium naphthenate in this work) in hydroponics culture, affected a total ion uptake by tomato plants. Increases in the uptake of nitrogen, phosphorus, iron, and copper were observed (Adani et al., 1998) and among them an increased Fe content in the plant roots was especially pronounced, similar to our results.

CONCLUSION

Experiments showed that there exists a possibility of increasing contents of some essential elements in plants treated with sodium naphthenate without changing concentration of these elements in the nutrient solution. Especially interesting results were obtained in the case of carrot, as increased contents were observed in the elements that are usually deficient (Fe, Zn, Mn), whereas the other remained unchanged. This opens up the possibility of using treated carrot with increased contents of these mineral essential elements in combating micronutrient malnutrition, bearing especially in mind that this vegetable is very widespread in diets (Ali and Tsou, 1997).

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POVEĆANJE SADRŽAJA MIKRONUTRIJENATA KOD CELERA, MRKVE, PAŠTRNAKA I PERŠUNA NAKON TRETMANA NATRIJUM-NAFTENATIMA

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Izvod: Mlade biljke celera, peršuna, paštrnaka i mrkve uzgajane u hranjivom rastvoru tretirane su natrijum-naftenatom u koncentraciji 10^{-7} mol dm^{-3} folijarno i preko korena, uključivanjem u hranjivi rastvor. Oba tretmana uticala su na sadržaj svih ispitanih elemenata prisutnih u hranjivom rastvoru, ali na različit način, u zavisnosti od biljne vrste. Srednja promena (povećanje/smanjenje) u sadržaju ispitanih elemenata je bila oko 35%. Kod oba tretmana povećani sadržaj Fe je nađen kod mrkve i peršuna. Kod paštrnaka i celera nađeno je sniženje sadržaja Fe kod tretmana preko korena kao i sniženje sadržaja Mn kod oba tretmana.

Ključne reči: *esencijalni elementi, celer, mrkva, paštrnak, peršun.*

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