ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 18, No. 4 2011

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COMPARISON OF THE EFFECT OF MINERAL AND ORGANIC FERTILIZATION ON THE COMPOSITION OF AMINO ACIDS IN GREEN BIOMASS MAIZE

PORÓWNANIE WPŁYWU MINERALNEGO I ORGANICZNEGO NAWOŻENIA NA SKŁAD AMINOKWASÓW W ZIELONEJ MASIE KUKURYDZY

Abstract: The research aimed at an assessment of the effect of mineral and organic fertilization on the composition of amino acids in maize San c.v. The investigations were conducted as a pot experiment. The experimental design comprised 11 treatments differing with the dose and kind of supplied fertilizers. Mineral salts (NPK), farmyard manure, compost, municipal and industrial sewage sludges were used as the source of nutrients for maize. Two levels of NPK fertilization were considered in the experiment. Doses of farmyard manure, compost, municipal and industrial sludge were established on the basis of nitrogen fertilization level. Determined were 17 amino acids: theronine, leucine, phenylalanine, histidine, lysine, methionine, arginine, valine, isoleucine, tyrosine, cysteine, aspargine and glutamine acids, serine, proline, glicyne and alanine. Analysis of the obtained results showed that mineral fertilization much more differentiate the content of amino acids in maize than the organic treatment. In the case of organic fertilization the highest total content of amino acids in plant was obtained in the variant with a double dose of municipal sludge. The highest concentrations of exogenic amino acids was registered in maize fertilized with a double NPK dose, the lowest in plants fertilized with a single dose of compost. Among the exogenic amino acids leucine prevailed in the yields from all fertilizer treatments. It was demonstrated that methionine was the limiting amino acid.

Keywords: amino acids, farmyard manure, compost, sewage sludges, NPK, maize

One of the important parameters of plant yield assessment is biological value of protein determined on the basis of its amino acid composition [1, 2]. It has been commonly known that the value depends primarily on the content of exogenic (indispensable) amino acids, which animal organism cannot synthetize. The exogenic amino acids for animals are: phenylalanine, leucine, isoleucine, lysine, methionine, treonine, tryptophan, valine, histidine and arginine [3]. Insufficient content of even one of the above-mentioned amino acids in animal feed causes that the other are not

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assimilated by the organism at all or only to a small extent. The factors shaping both the crop yield and the share of individual amino acids in plant protein include fertilization, ie the kind and method of fertilizer application (mineral, natural or organic fertilizers) and the amount of applied doses [4–6]. Rational mineral and organic fertilization determines production of adequate quality yields and protects the soil and water environment against degradation. Additionally, a deficit of organic fertilizers necessitates the use of some wastes as unconventional fertilizers in agriculture [7]. According to Mazur [8] and Sita and Wasiak [9] the management of organic, chemically and biologically uncontaminated wastes in agriculture is of crucial importance for the natural environment and ecology and is the most rational way of their utilization. Undoubtedly, the important advantage of organic material is the fact that they contain nutrients, crucial for plants, are good substrate for soil humus formation, whereas their fertilizer effect, especially in case of compost, is prolonged in time [10]. The paper aimed at an assessment of mineral and organic fertilization on the composition of amino acids in maize.

Material and methods

The investigations of the effect of mineral and organic fertilization on amino acid composition in maize were conducted as a pot experiment. Maize (*Zea mays* L.), San c.v. was the test plant. The experiment was set up on the soil with granulometric structure of weakly loamy sand and pH_{KCl} 4.66. The analyzed soil contained: 11.2 $g \cdot kg^{-1}$ organic carbon, 1.0 $g \cdot kg^{-1}$ nitrogen, 7.2 mg $P_2O_5 \cdot kg^{-1}$ and 17.3 mg $K_2O \cdot kg^{-1}$ d.m. The experimental design comprised 11 treatments in four replications differing with a dose and kind of supplied fertilizers (Table 2). The source of nutrients were: mineral salts, farmyard manure, compost, municipal and industrial sewage sludge. Two doses of NPK fertilization were considered in the experiment. On dose I 0.55 g N, 0.22 g P, 0.52 g $K \cdot pot^{-1}$ were used, dose II corresponded to 1.10 g N, 0.44 g P and 1.04 g $K \cdot pot^{-1}$. Doses of farmyard manure, compost, municipal and industrial sewage sludge were determined on the basis of nitrogen fertilization assumed for mineral treatments.

Table 1

Chemical composition of organic materials

Chemical composition		Farmyard manure	Compost	Municipal sludge	Industrial sludge
Dry mass	%	14.56	54.72	18.81	21.84
Organic mater	$g \cdot kg^{-1}$ d.m.	855.3	437.3	640.4	482.8
C-Organic		413.6	253.60	371.47	280.0
N		20.9	26.40	40.10	28.80
P		4.50	5.10	16.00	8.60
K		19.70	13.40	3.50	2.30
$g \cdot pot^{-1}$					
1/2 dose		181.0/362.0	38.0/76.0	73.0/146.0	87.4/174.9

Technical NPK salts were supplied as water solutions of NH_4NO_3, KH_2PO_4 and KCl. Chemical composition and the doses of applied fertilizer components were presented in Table 1. Compost was manufactured from plant wastes by Ekokonsorcjum Efekt Ltd. in Krakow, whereas sewage sludges originated from "Empos" municipal-industrial sewage treatment plant in Oswiecim. Exceeded heavy metal concentrations were determined neither in compost nor in sludges, therefore these materials met the requirements for the fertilizers used in agriculture and land reclamation for agricultural purposes [11].

Harvesting maize was after 63 days vegetation in 8–10 leaves phase. After harvesting the plant material was dried and dry mass yield was assessed, as well as total N and protein N using Kjeldahl distilling method [12]. Amino acids were determined with ninhydrine method by AA-400 Ingos analyzer. Determined were 17 amino acids: theronine (Thr), leucine (Leu), phenyalanine (Phe), histidine (His), lysine (Lys), methionine (Met), arginine (Arg), valine (Val), isoleucine (Ile), tyrosine (Tyr), cysteine (Cys), aspargine (Asp) and glutamine (Glu) acids, serine (Ser), proline (Pro), glicyne (Gly) and alanine (Ala).

Results and discussion

Total contents of exogenic and endogenic amino acids in maize were presented in Table 2.

Table 2

Scheme of experiment and total amino acids content in the maize aboveground parts

Treatments		Amino acids sum		
		Egzogenic	Endogenic	Egzogenic + Endogenic
		mg · g^{-1} d.m.		
I	Without fertilization	13.31	16.92	30.23
II	NPK*	21.97	25.90	47.87
III	NPK**	27.83	35.97	63.80
IV	Farmyard manure*	14.14	16.41	30.55
V	Farmyard manure**	15.04	17.20	32.24
VI	Compost*	13.66	17.73	31.39
VII	Compost**	15.50	15.09	30.59
VIII	Municipal sludge*	16.00	18.25	34.25
IX	Municipal sludge**	20.81	23.96	44.77
X	Industrial sludge*	16.88	18.98	35.86
XI	Industrial sludge**	17.97	20.71	38.68

* dose I: 0.55 g N · pot^{-1}, ** dose II: 1.10 g N · pot^{-1}.

Percentage use of exogenic amino acids fluctuated from 44 % to 51 % depending on the treatment, whereas endogenic amino acids content was slightly higher and constituted between 49 % and 56 % of the total sum of these compounds. It was demonstrated that the applied fertilization affected an increase in amino acid sum

content in maize as compared with the control treatment. However, mineral fertilization contributed to the increase in endogenic and exogenic animo acids sum more than organic fertilization. Additionally, higher contents of amino acids were found in the treatments with the second fertilization level than the first. In the treatment with a double NPK dose both the contents of exogenic and endogenic amino acids raised over twice in comparison with the control. In case of organic treatment, the highest contents of exogenic and endogenic amino acids in maize were noted in treatments fertilized with a double dose of municipal sludge (Table 2). This increase was 56 % in relation to the control (for exogenic) and 42 % (endogenic) amino acids. The smallest content of amino acids was registered in biomass maize cultivated in treatment with a single dose of compost. Additionally on treatments receiving farmyard manure and compost, the contents of amino acids were on a similar level. Moreover, these fertilizers caused a slight increase in the content of amino acid sum, on average by 4 % (I fertilization level) and by 15 % (II level) in comparison with the unfertilized control.

Depending on the fertilizer treatment, the total contents of amino acid sum in maize may be put in the following order: farmyard manure ≈ compost < industrial sewage sludge < municipal sewage sludge < NPK.

Irrespective of the experimental treatment, leucine prevailed among the exogenic amino acids constituting on average 20 % of their total sum (Table 3).

Table 3

Egzogenic amino acid content in the maize aboveground parts

Treatments		Thr	Leu	Ile	Phe	His	Lys	Met	Arg	Val
		mg · g^{-1} d.m.								
I	Without fertilization	1.29	2.80	1.26	1.30	1.16	1.67	0.30	1.67	1.89
II	NPK*	2.33	4.29	2.07	2.30	1.68	2.71	0.56	3.11	2.92
III	NPK**	3.13	5.34	2.51	3.01	2.06	3.47	0.78	3.94	3.59
IV	Farmyard manure*	1.50	2.86	1.30	1.38	1.18	1.76	0.43	1.85	1.88
V	Farmyard manure**	1.56	3.03	1.44	1.49	1.25	1.85	0.41	1.96	2.05
VI	Compost*	1.38	2.85	1.31	1.30	1.14	1.68	0.36	1.79	1.85
VII	Compost**	1.58	3.15	1.43	1.48	1.30	1.88	0.44	2.17	2.07
VIII	Municipal sludge*	1.67	3.24	1.49	1.54	1.41	1.92	0.48	2.11	2.14
IX	Municipal sludge**	2.14	4.17	2.02	2.08	1.68	2.53	0.53	2.83	2.83
X	Industrial sludge*	1.74	3.43	1.63	1.66	1.41	2.02	0.48	2.21	2.30
XI	Industrial sludge**	1.92	3.70	1.60	1.82	1.54	2.28	0.43	2.35	2.33

* dose I: 0.55 g N · pot^{-1}, ** dose II: 1.10 g N · pot^{-1}.

It was demonstrated that methionine was the amino acid limiting protein value. Percentage use of Met in total contents of exogenic amino acids was 3 %. Percentage of exogenic amino acids in the amino acids sum were as follows: Leu (20 %) > Arg (13 %) ≈ Val (13 %) > Lys (12 %) > Thr (10 %) ≈ Phe (10 %) >Ile (9 %) > Hist (8 %) > Met (3 %). Higher content of individual exogenic amino acids was registered in minerally than in organically fertilized maize, but the treatments receiving a double NPK dose had

the highest contents of the analysed amino acids. On the other hand, while estimating the organically fertilized treatments, the highest content of treonine and leucine in maize were found on the treatments where a double dose of municipal sewage sludge was used, whereas the greatest amounts of the other exogenic amino acids were noted in maize fertilized with a double dose of municipal sewage sludge. Moreover, slightly lower contents of individual exogenic amino acids were assessed in maize fertilized with farmyard manure and compost than with sewage sludges (Table 3).

The contents of analyzed endogenic amino acids in maize were presented in Table 4. As regards the endogenic amino acids the highest content in maize was registered for glutamine acid, which made up 23 % of the total content of endogenic amino acids. The contents of endogenic amino acids may be put in the following order: Glu (23 %) > Asp (18 %) > Ala (16 %) > Pro (14 %) > Gly (10 %) > Ser (9 %) > Tyr (7 %) > Cys (3 %). Higher content of individual endogenic amino acids was found in maize fertilized with a double NPK dose. On the other hand, among the organically fertilized treatments, maize cultivated on the treatment with a double dose of municipal sewage sludge revealed the highest content of the analyzed amino acids (Table 4). Compost applied in a single dose affected a decrease in the content of analyzed amino acids from 9 % to 29 % in relation to the control.

Table 4

Endogenic amino acid content in the maize aboveground parts

Treatments		Asp	Ser	Glu	Pro	Gly	Ala	Tyr	Cys
		mg · g^{-1} d.m.							
I	Without fertilization	3.03	1.58	3.83	2.25	1.77	2.75	1.20	0.51
II	NPK*	4.81	2.34	5.81	3.75	2.62	4.21	1.71	0.65
III	NPK**	7.85	3.44	7.86	4.93	3.55	5.58	1.93	0.83
IV	Farmyard manure*	2.91	1.55	3.74	2.28	1.73	2.67	1.11	0.42
V	Farmyard manure**	3.06	1.62	3.88	2.41	1.82	2.86	1.15	0.36
VI	Compost*	2.73	1.43	3.45	1.95	1.61	2.51	1.05	0.40
VII	Compost**	3.19	1.69	4.09	2.34	1.86	2.91	1.18	0.47
VIII	Municipal sludge*	3.25	1.72	4.08	2.59	1.92	2.92	1.28	0.49
IX	Municipal sludge**	4.42	2.18	5.34	3.62	2.45	3.86	1.54	0.55
X	Industrial sludge*	3.43	1.73	4.30	2.52	2.04	3.13	1.33	0.50
XI	Industrial sludge**	3.82	2.04	4.80	2.61	2.23	3.37	1.27	0.57

* dose I: 0.55 g N · pot^{-1}, ** dose II: 1.10 g N · pot^{-1}.

Fertilization greatly affects the structure of yields and considerably modifies the contents of amino acids in plants [13, 14]. Research conducted by Nowak and Majcherczak [14] demonstrated that application of only mineral fertilization leads to a decline in the contents of majority of amino acids in plant total protein in comparison with treatment unfertilized with NPK or farmyard manure. In the studies of Czuba and Mazur [15] exogenic amino acid contents decreased in result of nitrogen fertilization, except for phenylalanine and leucine. Nitrogen fertilization also contributes to decreas-

ing lysine content [16]. On the other hand Domska et al [2] found a higher content of exogenic amino acids in protein of barley grain under the influence of organic-mineral fertilization with copper and zinc supplement. The research of Jasiewicz et al [17] revealed that plants fertilized with various materials and organic wastes contained much more exogenic amino acids than those receiving mineral fertilizers, however leucine prevailed on all treatments. In the presented experiment a higher content of exogenic and endogenic amino acids was registered in maize fertilized minerally (a single and double NPK dose) than organically. The similar examination received in content of total and protein nitrogen in maize, presented in the previous publication [12]. It was also showed that higher contents of these parameters in minerally than organically fertilized plants. Moreover, as has been emphasized in the introduction, feed protein value is primarily determined by its composition of amino acids. In view of nutritional value, a group of amino acids indispensable for animal organisms (exogenic) has been identified in proteins. Among them the most important are limiting amino acids, ie those whose amounts are the lowest in relation to animal needs, these include lysine and methionine [3]. According to Rogalski [18] protein of grasses used for fodder reveals considerable deficiency of methionine and the content of this amino acid limits its value. Presented research also found that maize on all fertilizer treatments revealed the lowest content of this amino acid.

Conclusions

1. Mineral fertilization affected an increase in the total contents of amino acids to a greater degree in comparison with organic fertilization and control treatment.
2. In case of organic fertilization the highest total contents of amino acids in the maize aboveground parts was obtained in the variant with a double dose of municipal sludge.
3. The highest content of exogenic and endogenic amino acids in maize was registered on treatments fertilized with a double NPK dose and the lowest in plants receiving a single dose of compost.
4. Leucine prevailed among all exogenic amino acids in the protein maize aboveground parts from all fertilizer treatments, whereas glutamine acid among the endogenic amino acids.
5. It was demonstrated that methionine was the amino acid limiting protein value.

References

[1] Nowak K. and Majcherczak E.: Zesz. Probl. Post. Nauk. Roln. 2002, **484**, 441–449.
[2] Domska D., Wojtkowiak K., Warechowska M. and Raczkowski M.: Zesz. Probl. Post. Nauk. Roln. 2003, **494**, 99–104.
[3] Jamroz D. (ed.): Żywienie zwierząt i paszoznawstwo, Cz. III. Wyd. Nauk. PWN, Warszawa 2001, pp. 407.
[4] Czuba R.: Zesz. Probl. Post. Nauk Roln. 1996, **440**, 65–73.
[5] Klupczyński Z.: *Wpływ nawożenia azotem na plon i jakość ziarna zbóż*. Mat. Symp.: Wpływ nawożenia na jakość plonów, 24–25 VI 1986, Olsztyn, 82–102.
[6] Mazur T. and Sądej W.: Zesz. Probl. Post. Nauk. Roln. 2002, **484**, 377–384.

[7] Mazur T.: Zesz. Probl. Post. Nauk Roln. 1999, **467**, 151–157.
[8] Mazur T.: Acta Agrophys. 2002, **70**, 257–263.
[9] Siuta J. and Wasiak G.: *Zasady wykorzystania osadów ściekowych na cele nie przemysłowe (przyrodnicze)*. Inż. Ekol. 2001, **3**, 13–42.
[10] Gambuś F. and Wieczorek J.: Zesz. Probl. Post., Nauk Roln. 1999, **467**, 513–520.
[11] Rozporządzenie Ministra Środowiska z dnia 1 sierpnia 2002 r. w sprawie komunalnych osadów ściekowych. DzU. nr 134, poz. 1140.
[12] Jasiewicz Cz. and Antonkiewicz J.: Wpływ dawki i rodzaju nawozu na zawartość azotu w kukurydzy. Mat. Pokonf.: Zanieczyszczenia środowiska azotem. Monografie Wszechnicy Mazurskiej w Olecku, Olsztyn 2005, 143–152.
[13] Majcherczak E., Cwojdziński W. and Nowak K.: Acta Sci. Polon., Agriculture 2003, **2**(2), 11–18.
[14] Cwojdziński W. and Nowak K.: Zesz. Nauk. AR Szczecin 2000, **211**, 63–84
[15] Czuba R. and Mazur T.: Wpływ nawożenia na jakość planów. Wyd. Nauk. PWN, Warszawa 1988.
[16] Krasnodębska I. and Korelewski J.: Rocz. Nauk. Zootech. 1975, **2**(2), 209–219.
[17] Jasiewicz Cz., Antonkiewicz J. and Baran A.: Zesz. Probl. Post. Nauk Roln. 2006, **513**, 149–159.
[18] Rogalski M. (ed.): Łąkarstwo. Wyd. Kurpisz, Poznań 2004, pp. 271.

PORÓWNANIE WPŁYWU MINERALNEGO I ORGANICZNEGO NAWOŻENIA NA SKŁAD AMINOKWASÓW W ZIELONEJ MASIE KUKURYDZY

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Abstrakt: Celem badań była ocena wpływu nawożenia mineralnego i organicznego na skład aminokwasów w kukurydzy odmiany San. Badania prowadzono w warunkach doświadczenia wazonowego. Schemat doświadczenia obejmował 11 obiektów różniących się dawką oraz rodzajem wprowadzonych nawozów. Stosowano dwa poziomy nawożenia NPK. Jako źródło składników pokarmowych dla kukurydzy zastosowano sole mineralne (NPK), obornik, kompost, osad ściekowy miejski i przemysłowy. Dawki obornika, kompostu oraz miejskiego i przemysłowego osadu ściekowego ustalono na podstawie poziomu nawożenia azotowego przyjętego w obiektach z nawożeniem mineralnym. Oznaczono 17 aminokwasów: treoninę, leucynę, fenyloalaninę, histydynę, lizynę, metioninę, argininę, walinę, izoleucynę, tyrozynę, cysteinę, kwas asparaginowy i glutaminowy, serynę, prolinę, glicynę i alaninę. Analizując otrzymane wyniki stwierdzono, że nawożenie mineralne w większym stopniu różnicowało zawartość aminokwasów w kukurydzy w porównaniu z nawożeniem organicznym. W przypadku nawożenia organicznego największą zawartość ogólną aminokwasów w roślinie uzyskano w wariancie z osadem miejskim zastosowanym w podwójnej dawce. Największą zawartość aminokwasów egzogennych stwierdzono w kukurydzy nawożonej podwójną dawką NPK, najmniejszą zaś w roślinach nawożonych kompostem w pojedynczej dawce. Spośród aminokwasów egzogennych w plonach ze wszystkich obiektów nawozowych przeważała leucyna. Wykazano, że aminokwasem limitującym była metionina.

Słowa kluczowe: aminokwasy, obornik, kompost, osady ściekowe, NPK, kukurydza