Journal of Elementology ISSN 1644-2296

Symanowicz B. 2020.
Antagonistic changes in the content of molybdenum and boron in field pea and in soil under of the influence potassium fertilisation.
J. Elem., 25(1): 193-203. DOI: 10.5601/jelem.2019.24.4.1897

RECEIVED: 6 August 2019
ACCEPTED: 6 October 2019

ORIGINAL PAPER

ANTAGONISTIC CHANGES IN THE CONTENT OF MOLYBDENUM AND BORON IN FIELD PEA AND IN SOIL UNDER OF THE INFLUENCE POTASSIUM FERTILISATION*

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Abstract

The effect of potassium fertilisation on the molybdenum and boron content and uptake by field pea organs was investigated. The field experiment was established at the experimental unit of the Siedlce University of Natural Sciences and Humanities. The experimental design was a completely randomised arrangement with four repetitions. The first factor included five levels fertilisation with potassium (NK0 – 0, NK1 – 41.5, NK2 – 83, NK3 – 124, NK4 – 166, NK5 – 207.5 kg ha^{-1}), and the second factor consisted of two years of research (2011 and 2012). Every year in spring, nitrogen was applied in the quantity of 20 kg ha^{-1}. There was no phosphorus application (a very high content of available phosphorus in the soil). The applied potassium fertilisation significantly differentiated the molybdenum and boron content of the field pea seeds, straw, deseeded pods and roots. The study determined the highest molybdenum content (7.71 mg kg^{-1} DM) in the field pea seeds collected from the plots fertilised with NK1, and the greatest boron content in deseeded pods (27.41 mg kg^{-1} DM) collected from the plots fertilised with NK2. The lowest molybdenum content was determined in deseeded pods, and the lowest boron content was in the field pea seeds. The average molybdenum content (in mg kg^{-1} DM) in test plants can be presented in the following decreasing order: seeds (6.79) > roots (1.99) > straw (1.47) > deseeded pods (1.39), and for boron: deseeded pods (24.34) > straw (20.15) > roots (15.56) > seeds (7.53). The total molybdenum content of the soil ranged from 0.11 to 0.15, and the total boron content ranged from 2.70 to 3.23 mg kg^{-1} soil.

Keywords: pea, potassium fertilisation, molybdenum, boron, uptake, soil.

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* The results of the research carried out under the research project No 315/12/S were financed from the science grant granted by the Ministry of Science and Higher Education.

INTRODUCTION

In properly managed plant production, element deficits in soil and in plants should not occur. Regular application of natural and organic fertilisers, as well as the cultivation of legume family plants (Kozak, Kotecki 2006, Swędrzyńska et al. 2013, Małecka-Jankowiak et al. 2016), can completely satisfy the plants' demand for micronutrients (Symanowicz et al. 2012). Molybdenum and boron are micronutrients that are necessary for the plant growth and development and are essential for animals (Spiak 2000, Popova et al. 2017). According to Spiak (2000), these elements are antagonistic to potassium. These elements are particularly important due to their physiological role. They are a comopnent of numerous enzymes, are involved in amino acid biosynthesis and participate in N_2 fixing and the photosynthesis process (Peoples et al. 1995, Symanowicz et al. 2014).

Potassium fertilisers have an advantageous effect on the intensification of carbohydrate transformations, and activate the enzymes necessary for protein formation. However, the application of excessively high doses may result in ionic antagonism between potassium and molybdenum and boron. Organic matter and free carbonates increase the molybdenum availability to plants, and the organic matter content of the soil may be a safe pool of boron in the soil. In plants, molybdenum is found at the lowest concentrations of all micronutrients. Molybdenum is taken up by plants in the form of MoO_4^{2-}. It is involved in the reduction of (V) to (III) nitrates, it is a component part of nitrates (V) reductase, and it also engaged in N_2 fixing by both nodule and free-living bacteria (it is included in nitrogenase).

Molybdenum also participates in the phosphate metabolism and the synthesis of proteins and ascorbic acid. The molybdenum content of plants increases with the reduction in soil pH. The average molybdenum content of plants ranges from 0.1 to 6 mg kg^{-1} DM, but for the legume family plants from 0.02 to 3.56 mg kg^{-1} DM, and on average it equals 0.5 mg kg^{-1} DM (Rutkowska et al. 2017). A study by Symanowicz, Kalembasa (2012) determined the molibdenum content at a level of 4.27, 4.44 and 3.67 mg kg^{-1} DM in subsequent cuts of fodder galega (*Galega orientalis*, a small-seeded legume family plant) collected in the budding phase. Boron is involved in carbohydrate transformations. Recent research indicates that boron participates in the biological reduction of molecular nitrogen.

Under the conditions of the application of increased potassium fertiliser doses at a low soil richness in available potassium, it is necessary to monitor the content of these elements due to a risk of their deficit. However, there are no data concerning the qualitative and quantitative changes in the molybdenum or boron content of field pea or in soil in response to fertilisation with different potassium doses.

The aim of the study was to determine changes in the molybdenum and boron content of field pea (*Pisum sativum* L.) and of soil as affected by fertilisation with different potassium doses.

MATERIAL AND METHODS

A field experiment was conducted over two years at the experimental unit of Siedlce University of Natural Sciences and Humanities (52°17′ N; 22°28′ E). The experiment was designed as a completely randomised arrangement with four replicates, and it included two factors: factor I comprised five levels of potassium fertilisation (NK0 – 0, NK1 – 41.5, NK2 – 83, NK3 – 124, NK4 – 166, NK5 – 207.5 kg ha^{-1}), factor II included two years of research (2011 and 2012). Every year in spring nitrogen was used in a dose of 20 kg ha^{-1} (ammonium nitrate 34%) in addition to potassium (potassium salt 60%). No phosphorus was applied owing to a very high content of available phosphorus in the soil. The soil was characterised by a low content of available potassium form. The content of available forms of phosphorus and potassium in the soil was determined by the Egner-Riehm method according to the norms PN-R-04023:1996 and PN-R-04022:1996. The soil in the experiment was classified as loamy sand – LS *(Polish Soil Classification* 2011). The study was conducted at the same location in each year (soil pH – 6.9-7.04 measured in mol KCl dm^{-3}, total carbon – 37 g kg^{-1}, total nitrogen – 2.1 g kg^{-1}).

Test plants from individual fertilisation treatments were collected from an area of 1 m^2, their yield was estimated, after which they were dried and then divided into seeds, straw, pods and roots. Samples of soil from the humus horizon were taken four times (April, May, June, July) and subsequently dried and sifted through a 1 mm mesh sieve.

The amounts of molybdenum and boron analysed in the pea plant organs and in soil were determined by the ICP-AES method. The content of the microelements in field pea (seeds, straw, pods, and roots) and soil was established after dry mineralisation of the samples at a temperature 550°C. The resultant ash was dissolved in a solution of hydrochloric acid ($HCl : H_2O$, 1 : 1) and evaporated until dry to decompose carbonates and separate silicates and ash dissolved in 10% HCl.

The results of the experiments were analysed by ANOVA. Significance of sources of variation was checked with the Fisher-Snedecor test, and mean values were separated at the significance level of $p \leq 0.05$. Linear regression analysis and an analysis of correlation coefficients were performed for the amounts of the microelements. All calculations were made using Statistica ver. PL 12 (Statsoft. Inc. 2019).

RESULTS AND DISCUSSION

Different potassium doses applied in the study had a significant effect on the molybdenum content of the seeds, straw, deseeded pods and roots of field pea (Table 1). A significant reduction in the molybdenum content of

Table 1

Content of molybdenum in pea (mg kg^{-1} DM)

Fertilisation objects	Seeds			Straw			Pods			Roots		
	research of years											
	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean
NK0	8.17	7.08	7.62	1.19	1.77	1.48	1.70	1.32	1.51	1.77	1.81	1.79
NK1	7.11	8.32	7.71	1.82	1.43	1.62	1.88	1.72	1.80	2.01	2.28	2.15
NK2	8.07	7.18	7.62	1.22	1.90	1.56	1.65	1.16	1.40	2.88	2.48	2.68
NK3	5.72	6.24	5.98	1.66	1.41	1.53	1.28	1.24	1.26	1.84	1.35	1.60
NK4	4.91	6.19	5.55	1.26	1.30	1.28	1.57	1.37	1.47	1.82	1.70	1.76
NK5	5.54	5.60	5.57	0.81	1.09	0.95	0.95	0.96	0.96	2.20	1.70	1.95
Mean	6.59	6.76	6.68	1.32	1.48	1.40	1.50	1.29	1.40	2.08	1.89	1.99
$LSD_{0.05}$ for:												
fertilisation (F)			1.12			0.63			0.55			0.68
years (Y)			n.s.			n.s.			0.21			n.s.
interaction (YxF)			1.03			n.s.			n.s.			n.s.
(FxY)			1.59			n.s.			n.s.			n.s.

Explanation: N – 20, K1 – 41.5, K2 – 83, K3 – 124, K4 – 166, K5 – 207.5 kg ha^{-1}

seeds (by 21.52, 27.17 and 26.90%) compared to the control object was noted after the application of potassium salt in doses of 124, 166 and 207.5 kg ha^{-1}. The molybdenum content in pea seeds was twice as high as the acceptable standard content of this component in fodder plants (Gorlach 1991). Also, the use of sludge at doses 10, 20, 40, and 60 Mg ha^{-1} significantly increased the content of molybdenum in *Rosa multiflora* and *Sida hermaphrodita* (Antonkiewicz et al. 2019). The highest amount of molybdenum (1.62 mg kg^{-1} DM) was determined in pea straw after the application of potassium at a dose of 41.5 kg ha^{-1}. Similar content of molybdenum was determined in the biomass of eastern galega grown in the third year of cultivation, in subsequent development phases (Kalembasa, Symanowicz 2009). A significant reduction in this micronutrient in straw was noted after the application of the highest potassium dose (207.5 kg ha^{-1}). A similar relationship was observed for deseeded pods. In the deseeded pods collected from plots fertilised with the highest potassium dose, the molybdenum content decreased by 36.42% compared to the control object. In the roots of the test plants, the molybdenum content increased after the application of potassium at a dose of 41.5 and 83 kg ha^{-1}. Subsequently higher doses (124, 166 and 207.5 kg ha^{-1}) contributed to a significant reduction in molybdenum in the roots. A statistically significant reduction in the molybdenum content in the second year of the study was demonstrated. The results concerning the content of molybdenum in pea biomass were greater than the amount which Godlewska (2018) determined in the biomass of maize.

The study demonstrated significant changes in the boron content of straw, deseeded pods and the roots under the influence of the application of different potassium doses, and in the seeds and straw during the years of the study, and for the synergy of potassium fertilisation and the years of the study

Table 2

Content of boron in pea (mg kg^{-1} DM)

Fertilisation objects	Seeds			Straw			Pods			Roots		
	research of years											
	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean
NK0	6.24	8.50	7.37	16.74	25.44	21.09	28.12	25.84	26.98	14.53	14.48	14.50
NK1	7.92	8.53	8.22	21.31	20.44	20.87	23.49	25.71	24.60	16.03	14.48	15.26
NK2	6.59	8.53	7.56	19.26	21.61	20.43	29.03	25.80	27.41	16.14	17.88	17.01
NK3	4.93	9.75	7.34	19.82	21.69	20.76	23.23	19.50	21.36	14.21	14.75	14.48
NK4	6.39	9.92	8.15	18.21	20.61	19.41	23.80	25.20	24.50	14.99	16.45	15.72
NK5	5.97	10.57	8.27	15.77	19.19	17.48	21.05	18.02	19.53	14.90	15.23	15.06
mean	6.34	9.30	7.82	18.51	21.49	20.00	24.78	23.34	24.06	15.13	15.54	15.34
$LSD_{0.05}$ for:												
fertilisation (F)			n.s.			2.09			3.89			2.12
years (Y)			0.57			0.78			n.s.			n.s.
interaction (YxF)			1.39			1.92			n.s.			n.s.
(FxY)			2.15			2.95			n.s.			n.s.

Explanation see Table 1

(Table 2). The highest amount of boron was determined in deseeded pods (24.06 mg kg^{-1} DM), and the lowest concentrations was in seeds (7.82 mg kg^{-1} DM). A significant reduction in the boron content of straw was noted in the objects fertilised with potassium at a dose of 207.5 kg ha^{-1}. In deseeded pods, a significant decrease was noted in the boron content in the objects fertilised with potassium at doses of 124 and 207.5 kg ha^{-1} compared to the control object. In field pea seeds, a significant increase in the boron content appeared in the objects fertilised with potassium in the dose of 83 kg ha^{-1}. In the second year of the study, the boron content of seeds and pea straw significantly increased. Subsequently higher potassium doses applied in the second year of the study significantly contributed to an increased in the boron content of test plants.

The average total molybdenum uptake with field pea (*Pisum sativum* L.) seeds, straw and pods (dry matter yield), expressed as the product of the molybdenum content in particular plant parts (Table 1) and in the yield (Symanowicz et al. 2017), was 33.87 g ha^{-1} (Table 3). The highest amount of molybdenum was taken up by the test plants with the seed yield, and the lowest one – with the yield of deseeded pods (Table 3). The applied potassium fertilisation significantly differentiated molybdenum uptake with the seed and straw yield. The years of the study had a significant effect only on the molybdenum uptake with the field pea seed yield. The synergy of the analysed factors also significantly affected the molybdenum uptake with the field pea seed and straw yields. Potassium applied at a dose of 83 kg ha^{-1} significantly contributed to an increase in the molybdenum uptake with the seed yield. The subsequent increase in potassium doses resulted in a reduction in the molybdenum uptake. A significant reduction

Table 3

Uptake of molybdenum with pea yield (g ha^{-1})

Fertilisation objects	Seeds			Straw			Pods		
	research of years								
	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean
NK0	27.21	22.76	24.98	5.87	6.29	6.08	1.51	1.12	1.32
NK1	22.02	27.48	24.75	8.69	5.13	6.91	1.75	1.40	1.58
NK2	27.83	34.47	31.15	5.72	9.19	7.46	1.40	1.35	1.37
NK3	24.18	34.41	29.29	7.93	7.77	7.85	1.08	1.51	1.29
NK4	18.15	30.20	24.18	6.13	6.13	6.13	1.30	1.78	1.54
NK5	18.22	25.29	21.75	3.88	5.20	4.54	0.87	1.23	1.05
Mean	22.93	29.10	26.02	6.37	6.62	6.49	1.32	1.40	1.36
$LSD_{0.05}$ for:									
fertilisation (F)			4.66			2.75			n.s.
years (Y)			1.75			n.s.			n.s.
interaction (YxF)			4.28			2.53			n.s.
(FxY)			6.59			3.89			n.s.

Explanation see Table 1

in the molybdenum uptake with the straw yield was noted after the application of potassium at a dose of 207.5 kg ha^{-1}. The region of pea cultivation had little impact on its quantity yield (Księżak et al. 2018). The calculated molybdenum uptake with the yield of pea pods was similar to the values achieved from determination of this microelement taken up with rye yield (Rutkowska et al. 2017).

The highest boron uptake with the field pea dry matter yield was noted for straw, and the smallest was for deseeded pods (Table 4). Potassium fer-

Table 4

Uptake of boron with pea yield (g ha^{-1})

Fertilisation objects	Seeds			Straw			Pods		
	research of years								
	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean
NK0	20.77	27.36	24.06	82.88	90.82	86.85	25.02	21.70	23.36
NK1	24.56	28.13	26.34	102.06	72.94	87.50	21.84	20.96	21.40
NK2	22.60	40.95	31.76	90.46	104.78	97.62	24.54	30.11	27.32
NK3	20.82	53.76	37.29	94.64	120.20	107.42	19.53	23.52	21.52
NK4	23.59	48.38	35.98	88.63	97.08	92.85	19.75	33.20	26.47
NK5	19.61	47.71	33.66	76.17	92.07	84.12	19.03	22.80	20.92
Mean	21.99	41.05	31.52	89.14	96.31	92.72	21.62	25.38	23.50
$LSD_{0.05}$ for:									
fertilisation (F)			5.22			9.83			5.26
years (Y)			1.96			3.68			1.97
interaction (YxF)			4.79			9.02			4.83
(FxY)			7.39			13.90			7.44

Explanation see Table 1

tilisation at doses of 83, 124, 166 and 207.5 kg ha^{-1} significantly contributed to an increase in the boron uptake with the seed yield by 32, 55, 50 and 40%, respectively, compared to the control object. Potassium applied in doses of 83 and 124 kg ha^{-1} caused a significant increase in the boron uptake with the straw yield by 12% and 24%, respectively, compared to the control object. Boron uptake with the pea deseeded pod dry matter yield increased significantly by 17% as a result of potassium fertilisation at a dose of 83 kg ha^{-1}, compared to the uptake obtained for the control object. It should be assumed that these differences result from the content of available potassium in the soil and varietal traits of the pea, like other components of chemical composition (Radulov et al. 2011, Zia-Ul-Hag et al. 2013, Andrzejewska et al. 2015).

The average molybdenum content of Polish soils ranges from 0.2 to 4.0 mg kg^{-1} soil (Rutkowska et al. 2017). The total molybdenum content of the analysed soil was at a low level (0.13 mg kg^{-1}), and varied on the subsequent sampling dates during a field pea growing season (Table 5).

Table 5

Total content of molybdenum in the soil (mg kg^{-1}) during pea growing season

Fertili-sation objects	Date of sampling											
	April			May			June			July		
	research of years											
	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean
NK0	0.21	0.25	0.23	0.09	0.13	0.11	0.07	0.10	0.09	0.09	0.12	0.11
NK1	0.11	0.17	0.14	0.10	0.14	0.12	0.08	0.13	0.11	0.07	0.13	0.10
NK2	0.15	0.18	0.16	0.10	0.13	0.12	0.11	0.15	0.13	0.10	0.15	0.13
NK3	0.11	0.08	0.10	0.10	0.08	0.09	0.08	0.15	0.11	0.07	0.21	0.14
NK4	0.11	0.17	0.14	0.11	0.10	0.11	0.07	0.21	0.14	0.06	0.19	0.12
NK5	0.11	0.15	0.13	0.10	0.10	0.10	0.08	0.20	0.14	0.08	0.23	0.16
Mean	0.13	0.17	0.15	0.10	0.11	0.11	0.08	0.16	0.12	0.08	0.17	0.13
$LSD_{0.05}$ for:												
fertilisation (F)			0.06			0.02			n.s.			0.03
years (Y)			0.02			0.01			0.03			0.01
interaction (YxF)			n.s.			0.02			n.s.			0.02
(FxY)			n.s.			0.03			n.s.			0.04

Explanation see Table 1

The applied potassium significantly differentiated the molybdenum content of the analysed soil collected in April, May and July. A significant reduction in the molybdenum content of the soil collected in April, compared to the control object, was noted in the objects fertilised with potassium in subsequent doses, and in the soil samples collected in May at the object fertilised with potassium at a dose of 124 kg ha^{-1}.

The soil collected in July from the plots fertilised with 124 and 207.5 kg ha^{-1} contained significantly more molybdenum compared with the soil from the control object. The results of obtained in this experiment, concerning the total molybdenum content of the soil, were higher by 62.5% than the molybdenum content determined by Symanowicz, Kalembasa (2012). Rutkowska et al. (2014) determined small amounts of molybdenum available to plants in the soil: 0.019 mg kg^{-1} molybdenum in the extract of 1 mol HCl dm^{-3} and 0.025 µmol dm^{-3} molybdenum in the soil solution. In the determination of molybdenum in soil the method adsorptive catalytic stripping voltammetry in the presence of Alizarin Red S (ARS) in the complex in the presence of persulphate as oxidizing reagent.proposed by Nakiboglu et al. (2011).

The study showed significant differences in the boron content of the soil collected in May and July resulting from potassium fertilisation (Table 6).

Table 6

Total content of boron in the soil (mg kg^{-1}) during pea growing season

Fertilisation objects	Date of sampling											
	April			May			June			July		
	research of years											
	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean	1st	2nd	mean
NK0	4.04	2.17	3.10	3.73	2.82	3.28	3.56	2.63	3.09	3.77	1.87	2.82
NK1	4.42	1.62	3.02	3.81	1.96	2.88	3.43	1.86	2.65	3.89	1.32	2.60
NK2	3.87	1.58	2.72	3.31	2.31	2.81	3.88	1.66	2.77	4.12	2.00	3.06
NK3	3.68	1.71	2.69	3.49	1.40	2.44	3.70	1.49	2.59	4.62	2.74	3.68
NK4	4.71	1.93	3.32	3.87	2.86	3.37	4.01	1.65	2.83	5.22	2.65	3.93
NK5	3.67	2.14	2.90	3.98	1.83	2.90	3.06	1.65	2.35	4.46	1.49	2.97
Mean	4.06	1.85	2.96	3.70	2.19	2.95	3.60	1.82	2.71	4.34	2.01	3.18
$LSD_{0.05}$ for:												
fertilisation (F)			n.s.			0.73			n.s.			0.97
years (Y)			0.51			0.28			0.27			0.36
interaction (YxF)			n.s.			0.67			0.66			n.s.
(FxY)			n.s.			1.04			1.01			n.s.

Explanation see Table 1

Significant differences were also noted during the years of the study for all soil sampling dates. Potassium applied at a dose of 124 kg ha^{-1} contributed to a reduction in the boron content of the soil in May by 25.6% compared to the boron content of the soil from the control object. In the research on the content of boron in orchard soils, significant and positive correlations were determined with the agronomic category and pH of soils. In the soil collected in May, there was a significant increase in the boron content of the soil (by 39.4%) under the influence of potassium applied at a dose of 166 kg ha^{-1} compared to the content in the soil not fertilised with potassium. Differences in the molybdenum and boron content in soil in subsequent months of the study probably resulted from high soil variability. Soil samples were taken from different locations on plots on the subsequent dates. During the second year of the study, the boron content of the soil decreased significantly compared to the first year on the subsequent dates of soil sampling and analysis. This was attributed to the removal of this element with the plant yield. The results of our research were similar ones concerning the content of boron in Polish soils (Szulc, Rutkowska 2013).

Table 7

Correlation coefficients between molybdenum (Mo) and boron (B) content in pea plant parts

Parameters	Mo_{se}	Mo_{st}	Mo_p	Mo_r	B_{se}	B_{st}	B_p	B_r
Mo_{se} #	-							
Mo_{st}	0.74	-						
Mo_p	0.68	0.77	-					
Mo_r	0.57	0.26	0.18	-				
B_{se}	-0.33	-0.53	0.01	0.08	-			
B_{st}	0.71	0.96*	0.74	0.06	-0.64	-		
B_p	0.77	0.65	0.68	0.49	0.37	0.67	-	
B_r	0.23	0.13	0.11	0.86*	0.15	-0.07	0.47	-

* The value of the correlation coefficient is significant at $p \leq 0.05$; # se – seeds, st – straw, p – pods, r – roots.

Based on the research conducted, significant relations were found between the molybdenum and boron content in the seeds (se), straw (st), pods (p) and roots (r) – Table 7. Values of correlation coefficients calculated during the statistical processing in most cases revealed significant dependencies between the factors studied in the experiment. Following were high values of correlation coefficients achieved in two cases: between Mo_{se} vs B_{st} and Mo_r vs B_r.

The statistical analysis demonstrated a significant relation between the content of molybdenum and boron in the dry matter of field pea straw (Figure 1*a*). A positive correlation between the molybdenum and boron con-

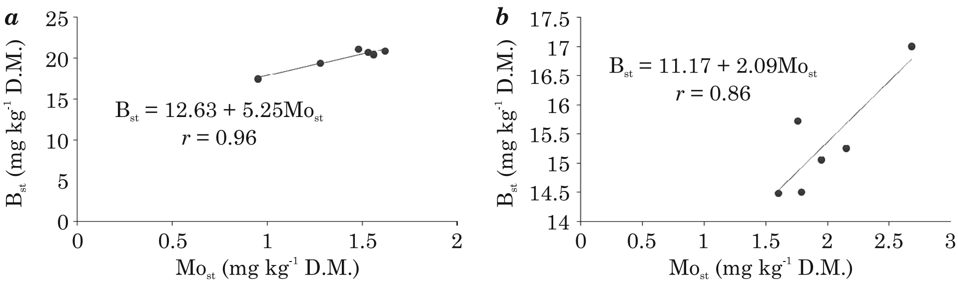

Fig. 1. Relationships between the molybdenum and boron content in pea straw (*a*), and in pea roots (*b*)

tent in the roots of pea was demonstrated for different potassium fertilisation variants (Figure 1*b*). The increase in the molybdenum content in the straw and roots of pea resulted in an increase of the boron content in the straw and roots.

CONCLUSIONS

The applied potassium fertilisation significantly differentiated the molybdenum and boron content of the field pea seeds, straw, deseeded pods and roots. The study determined the highest molybdenum content (7.71 mg kg^{-1} DM) in the field pea seeds collected from the plots fertilised with NK1, and the greatest boron content in deseeded pods (27.41 mg kg^{-1} DM) collected from the plots fertilised with NK2. The lowest molybdenum content was determined in deseeded pods, and the lowest boron content was in the field pea seeds.

The average molybdenum content (mg kg^{-1} DM) in test plants can be presented in the following decreasing order: seeds (6.79) > roots (1.99) > straw (1.47) > deseeded pods (1.39), and for boron: deseeded pods (24.34) > straw (20.15) > roots (15.56) > seeds (7.53). The total molybdenum content of the soil ranged from 0.11 to 0.15, and the total boron content ranged from 2.70 to 3.23 mg kg^{-1} soil.

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