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Prediction of molybdenum availability to plants in differentiated soil conditions

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ABSTRACT

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The aim of the study was to assess of plant available molybdenum (Mo) resources in the solutions of soils as well as to evaluate the effects of selected soil properties on changes of the Mo concentration in the soil solution. Sixty-two soil samples were investigated. The soil solutions were obtained by modified vacuum displacement method. The results showed that Mo concentrations in the soil solutions were much differentiated, ranging from 0.002 to approximately 0.100 μmol/L. Positive correlations were found between soil solution Mo concentration and soil pH as well as the contents of available phosphorous and organic carbon in soil. At the same time, Mo concentration was higher in the soil solutions obtained from soils with larger amounts of soil particles with diameter lesser than 0.02 mm. Among the analysed soil parameters in this study, soil pH is the most important factor that influences the Mo concentration in soil solution. Studies have shown that in acid sandy soils the amount of molybdenum found in the soil solution is too small to cover the nutritional requirements of the plants. This indicates the need of fertilization with this element. Regular liming of soils and fertilization with phosphorus can improve the availability of molybdenum to plants.

Keywords: micronutrient; mobility; leaching; solubility; acidic soils

Molybdenum (Mo) is an essential element for proper growth and development of the majority of living organisms, but it is required in very small amounts and has a narrow range between deficiency and toxicity. In plants, it plays a part in nitrogen metabolism as a component of enzymes such as nitrate reductase and nitrogenase. At the same time, Mo participates in the metabolism of sulphur, biosynthesis of plant hormones and catabolism of purine compounds (Kaiser et al. 2005).

Overall content of molybdenum in agricultural soils ranges from 0.2 to 5.0 mg/kg (Scheffer and Schachtschabel 2002). The plants take up Mo in the form of the molybdate anions (MoO_4^{2-} and $HMoO_4^-$) which are the predominant species in soil solution. A release of molybdenum from solid mineral forms to soil solution is determined by different soil properties, such as soil pH as well as soil content of Fe, Mn, Al oxides, clay minerals and organic carbon. Among these factors, soil pH has the strongest effect on the processes of adsorbing and releasing MnO_4^{2-} ions into the soil solution. The maximum adsorption of molybdenum onto positively charged metal oxides occurs between pH 4 and 5 (Riley et al. 1987, Xie et al. 1993, Gupta 1978, Xu et al. 2013). In acidic soils, molybdate

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anions are adsorbed onto positively charged Fe, Mn and Al oxides as well as clay minerals and organic colloids. Availability of molybdenum to plants increases together with increasing soil pH. For each unit of pH rise above 3, MoO_4^{2-} solubility increases about 100-fold, mainly through decreased adsorption of metal oxides (Smith et al. 1997, Jiang et al. 2015). The poorly drained wet soils, rich in organic matter tend to accumulate MoO_4 to high levels and from well-drained sandy soils molybdenum is readily leached away (Riley et al. 1987). The availability of Mo to plants primarily depends on the supply of soil available Mo and is also related to the species of plant (McGrath et al. 2010b).

The present study was undertaken with the aim to (i) assess the amount of easily available resources of molybdenum in the soil solutions of agriculturally used soils; (ii) evaluate the effects of some soil properties on changes of concentration of this element in the soil solution and (iii) determine the degree of supply of selected crop plants in Mo by the amount of this element that is in the soil solution.

MATERIAL AND METHODS

Sixty-two soil samples were collected by the Regional Agro-Chemical Laboratories from control points included in the system of the State Environmental Monitoring. The control points are located on arable land, characteristic for the soil cover of the country. One control point covers an area of 650 km^2. Depending on the area of agricultural land, 2 to 6 soil samples were collected from each voivodship. Soil samples were taken as follows: GPS-determined point was the central point of the square of 100 m^2, from which each individual sample was taken with a steel soil probe from a depth of 0–30 cm. The combination of individual samples was a collective sample representative of the control point. Soil samples were taken from the most common Polish soils: Haplic Luvisols, Haplic Cambisols, Haplic Arenosols with granulometric composition from loose sands to heavy loams.

The soils were air-dried, and ground in an agate mortar to pass through a 2.0 mm sieve for analysis.

Soil samples were characterized for: pH – by the potentiometric method after extraction with 1 mol/L KCl (10 g of soil was suspended in 25 mL of KCl and equilibrated for 24 h) using a pH meter (apparatus: Schott, Mainz, Germany); available P – by the Egner-Riehm (DL) method (Egner and Riehm 1958); available Mo – after extraction in 1 mol/L HCl (10 g of soil was shaken with 100 mL HCl on a rotary shaker for 2 h at 120 rounds per min) by the inductively coupled plasma-atomic emission spectrometry (ICP-AES, IRYS Advantage ThermoElementar, Cambridge, UK); total Mo by the *aqua regia* digestion, determined by the ICP-AES; total organic carbon content – by dry combustion at high temperatures in a furnace with the collection and detection of evolved CO_2 (Tiessen and Moir 1993); content of soil particles < 0.02 mm – by the laser diffraction method (Ryżak et al. 2007). In Poland, the content of soil particles < 0.02 mm determines the agricultural usefulness of soil. On this basis, four categories of soils are identified: very light (< 10% particles < 0.02 mm), light (10–20%), medium (20–35%) and heavy (> 35%).

The samples differed in terms of their physico-chemical properties, such as: content of soil particles < 0.02 mm, soil reaction, organic carbon content, available forms of molybdenum and phosphorus in soil (Table 1).

The soil solutions of all the observed soils were obtained by the modified vacuum displacement

Table 1. Properties of the investigated soils

Content of soil particles < 0.02 mm (%)	< 10 (17)	10–20 (17)	20–35 (17)	> 35
pH_{KCl}	< 4.5 (12)	4.6–5.5 (17)	5.6–6.5 (12)	> 6.6 (21)
Available phosphorus content in soil (mg/kg)	< 22 (7)	22–44 (15)	44–66 (12)	> 66 (28)
Soil organic carbon content (g/kg)	< 5 (3)	5–10 (30)	10–15 (25)	> 15 (4)
Available molybdenum content in soil (mg/kg)*	low (0.008–0.059) (42)		medium (0.026–0.070) (20)	
Total molybdenum content in soil (mg/kg)	< 0.5 (21)	0.5–1.0 (32)	1.0–1.5 (7)	> 1.5 (2)

*depending on soil pH and soil available phosphorus content in soil. Number of soils are in brackets

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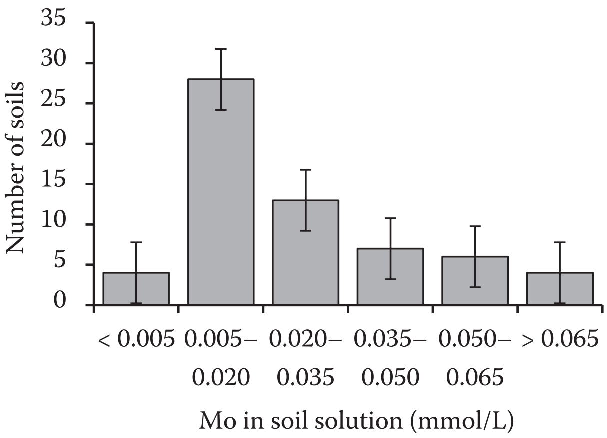
method of Wolt and Graveel (1986). Air-dried soil samples (100 g each) were wetted with redistilled water to 100% field water capacity and then incubated at room temperature for 72 h. Once the balance between solid and liquid soil phases was established, the soil solution was obtained with the use of a vacuum pump (Dynavac OP4, Melbourne, Australia) under pressure 0.08–0.09 MPa. The obtained soil solutions were filtered through a filter paper. The total concentration of Mo in soil solutions was determined by the inductively coupled plasma- atomic emission spectrometry (ICP-AES).

The ICP-AES apparatus calibration was made based on patterns prepared from the Single Element Standards for ICP Solution by Ultra Scientific company. To check the calibration curve, the solutions were used to check the instrument and the calibration (QC) at concentrations of 0.1 ppm and 1 ppm – before the samples were studied, and at every 20 samples according to the Combined Quality Control Standard from Ultra Scientific company.

Relationships between the concentration of Mo in the soil solution and selected soil properties were analysed with simple regression and correlation at a significance level $P = 0.05$. Statistical analyses were performed using the Statgraphics Plus Professional software (StatPoint Technologies, Inc., The Plains, Virginia, USA).

Relevant data on plant yields in Poland in the year 2015 (Concise Statistical Yearbook of Poland 2016) and average molybdenum contents in plants (Jadczyszyn 2000) were used in evaluating whether molybdenum quantity in the soil solution was sufficient for plant nutritional needs.



Minimum	Maximum	Mean	Standard deviation	Variation coefficient
0.0021	0.091	0.027	0.022	81.48

Figure 1. Range of soil solution molybdenum (Mo) concentration in agricultural soils in Poland

RESULTS AND DISCUSSION

The concentration of molybdenum in the soil solutions analysed ranged from 0.002 to 0.100 µmol/L and was differentiated depending on soil properties. Soil solution Mo concentration with range 0.005–0.035 µmol/L was found in 66% of all the analysed soils (Figure 1).

A similar range of Mo concentrations in the soil solutions of Poland's agricultural soils was earlier observed by Rutkowska (1999). Wolt (1994) reported that natural Mo concentration in the soil solution observed in the USA and Great Britain was 0.02 µmol/L. On the other hand, Balík et al. (2006) stated that Mo concentration in the soil solutions of agriculturally used soils ranged from 0.006 to 0.06 µmol/L.

Molybdenum concentration in the soil solutions analysed was determined by the properties of the observed soils. For strongly acidic (pH < 4.5) and

Table 2. Average soil solution molybdenum (Mo) concentration according as soil physico-chemical properties (µmol/L)

	Content of soil particles < 0.02 mm (%)			
	< 10	10–20	20–35	> 35
Mo	0.018	0.039	0.041	0.047
	pH_{KCl}			
	< 4.5	4.6–5.5	5.6–6.5	> 6.6
Mo	0.009	0.014	0.037	0.072
	available phosphorus content in soil (mg/kg)			
	< 22	22–44	44–66	> 66
Mo	0.011	0.015	0.017	0.048
	soil organic carbon content (g/kg)			
	< 5	5–10	10–15	> 15
Mo	0.007	0.021	0.041	0.056
	soil available Mo			
	low		medium	
Mo	0.023		0.045	

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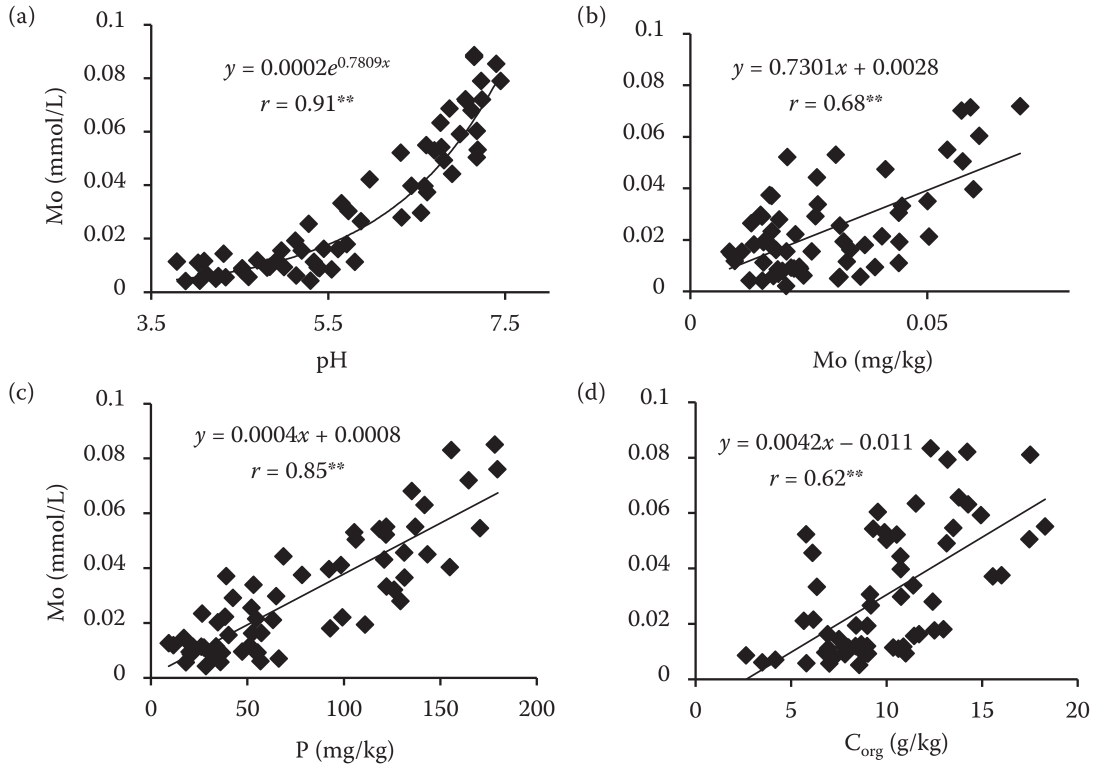

Figure 2. Relationship between soil solution molybdenum (Mo) concentration and (a) soil pH; (b) available Mo; (c) available phosphorus (P), and (d) organic carbon (C_{org}) content in soil. $^{**}P < 0.01$

acidic soils (pH 4.6–5.5), Mo concentration in the soil solution was lower than 0.02 μmol/L. It was significantly increased at rising soil pH values and reached on average 0.072 μmol/L in soils with neutral and alkaline soil pH (pH > 6.6) (Table 2, Figure 2a). In the soil solution of soils with pH value higher than 5.0 MoO_4^{2-} ions dominate. Above pH 4.2, MoO_4^- is the common anion followed in decreasing order by $MoO_4^- > HMO_4^- > H_2MO_4^0 > MoO_2(OH)_2^+ > MoO_2^{2+}$ (Lindsay 1979). In acidic soils with pH 4–5, molybdate anions are strongly adsorbed by positively charged oxides of Fe, Mn and Al, and this holds back availability of Mo for plants (Smith et al. 1997). With increasing soil pH the concentration of MoO_4^{2-} ions in the soil solution increases. As Lindsay (1979) and McGrath et al. (2010a) reported, for each unit of the pH value above 3.0, the concentration of molybdate ions can increase even one hundred times. Enhancement of Mo mobility in soil at high pH values is caused by an increase of free negative charges on soil colloids, stronger competition between molybdates and hydroxyl anions for adsorption sites, as well as by lower activity of Al and Fe oxides, which is the cause of reducing the amount of free positive sites able to adsorb molybdenum (Jarrell and Dawson 1978, Jiang et al. 2015).

The content of soil particles also determined Mo concentration in the soil solution. In heavy soils (> 35% of soil fractions < 0.02 mm), soil solution Mo concentration was more than two times higher when compared with that in very light soils (< 10% of soil fractions < 0.02 mm) (Table 2). Low Mo concentration in the soil solution of very light soils was connected with their strongly acidic soil reaction. On the other hand, soils with more than 35% content of fractions with particle diameter < 0.02 mm were characteristic of pH higher than 5.6. Studies of Jones and Belling (1967) showed enhanced molybdenum leaching in well-aired sandy soils. This process depends on soil pH. As indicated by Riley et al. (1987), molybdenum leaching from sandy soils with acidic soil reaction is limited because solubility of this element is restricted. The concentration of Mo in soil solution increased with the content of available molybdenum in soil (Figure 2b). The results of this study showed that with an increasing content of available phosphorous in soil the concentration of molybdenum in the soil solution increased, which was proven by

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correlation coefficient $r = 0.85$ (Figure 2c). Average molybdenum concentration in the soil solution depended on the content of available phosphorous in soil. In soils exceedingly rich in available phosphorous (> 66 mg/kg) soil solution Mo concentration was four times higher when compared with soils with low available phosphorous contents (< 22 mg/kg). In soil, phosphates compete with molybdates for adsorption sites on the surface of the solid soil layer, and with increasing available phosphorous amounts numerous adsorption sites with high affinity for molybdenum can be blocked by phosphates (Xie and MacKenzie 1991, Vistoso et al. 2009). As a result of this process, desorption of MoO_4^{2-} into the soil solution is enhanced. The process does not depend on soil reaction and is started in acidic soils. The soils tested were of low content of organic carbon. Nevertheless, significant relationships between soil solution Mo concentration and soil organic carbon contents were shown (Figure 2d).

In soils with organic carbon content > 15 g/kg, soil solution Mo concentration was eight times higher when compared with soils < 5 g/kg of organic carbon (Table 2). Studies on the effects of organic matter on molybdenum mobility are scarce and their results are not consistent. Kasimov et al. (2011) showed that the humus content in soil strongly affects molybdenum mobility. The strength of Mo absorption increased with higher humus in soil. Karimian and Cox (1978) and Xu et al. (2013) indicated that the soil solution Mo concentration decreased with increasing contents of organic carbon in soil, most probably as a result of formation of complexes with humic acids. On the other hand, Jenne (1977) as well as Reddy et al. (1997) showed that in the soil solution MoO_4^{2-} anions could form complex ions with metal cations (K, Na, Ca, Mg) and also with humic and fulvic acids. This influences indirectly the increase of molybdenum availability for plants through restraint adsorption of ions MoO_4^{2-} on Fe, Mn and Al oxides, especially in acidic soils.

Based on the multiple regression analysis, the relationship between the concentration of molybdenum in soil solution and the content of available molybdenum, available phosphorus and organic carbon in soil was significantly determined by

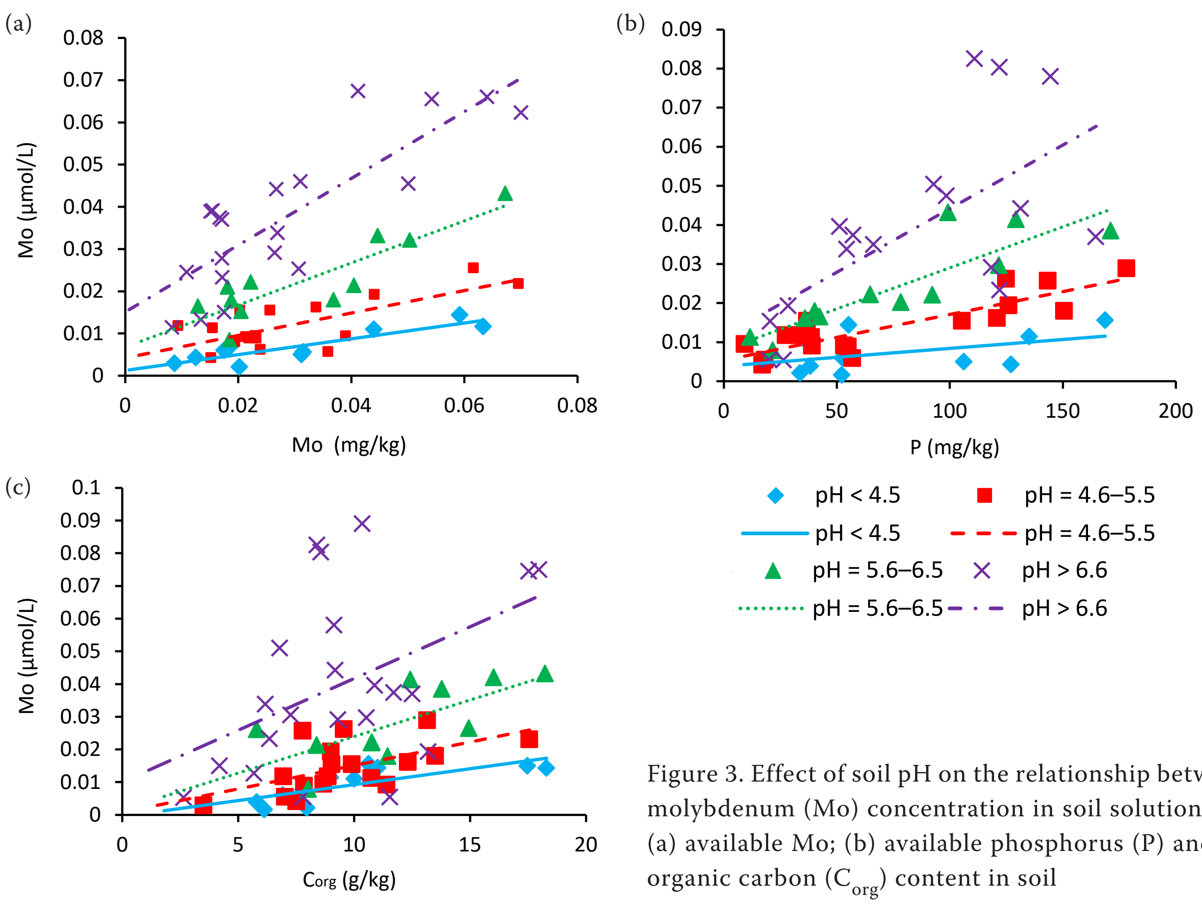

Figure 3. Effect of soil pH on the relationship between molybdenum (Mo) concentration in soil solution and (a) available Mo; (b) available phosphorus (P) and (c) organic carbon (C_{org}) content in soil

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Table 3. Regression equation between molybdenum (Mo) concentration in soil solution and selected soil properties

Dependent variable	Independent variable	Equation	P	R^2 (%)
	Mo available (Mo_{av}) soil pH	$Mo_{ss} = -0.06 + 0.51\ Mo_{av} + 0.11\ pH$	< 0.01	75.06
Mo soil solution (Mo_{ss})	P available (P_{av}) soil pH	$Mo_{ss} = -0.06 + 0.001\ P_{av} + 0.14\ pH$	< 0.01	56.23
	C_{org} soil pH	$Mo_{ss} = -0.06 + 0.002\ C_{org} + 0.01\ pH$	< 0.01	50.70

soil pH (Figure 3, Table 3). The concentration of molybdenum in the soil solution of strongly acidic soils was the smallest and significantly increased with the increase in the amount of molybdenum available in the soil. However, in soils with pH > 6.6, the concentration of molybdenum in the soil solution was significantly higher. Under such conditions, the increase in the amount of molybdenum available in the soil caused a much higher increase in the concentration of molybdenum in the soil solution than in strongly acidic soils (Figure 3a). Similar trends were found in the relationship between molybdenum concentration in soil solution and phosphorus content in soil (Figure 3b) and organic carbon content in soil (Figure 3c).

Average uptake of molybdenum by plants in Polish agriculture ranged from 1.68 to about 10 g per hectare (Table 4). The average content of active molybdenum in the arable layer of soil is sufficient to cover the nutritional needs only in the case of rye. This corresponds to a concentration of molybdenum in the soil solution at 0.027 μmol/L. 57% of the analysed soils are characterized by a concentration less than sufficient to cover the nutritional needs of plants (Figure 1).

The results of the study carried out indicate that molybdenum concentrations in the soil solutions of agriculturally used soils in Poland are very variable and depend on physico-chemical soil properties. A significant positive correlation was found between soil solution Mo concentration and soil pH, available phosphorous contents in soil as well as soil organic carbon contents. In the soil solution of soils with pH > 6.6, the concentration of Mo was eight times higher when compared with soils with pH < 4.5. Also an eight-fold increase of soil solution Mo concentration was observed under the influence of increased soil organic carbon contents from below 5 to more than 15 g/kg. At the same time, the concentration of molybdenum in the soil solutions increased in the observed soils with increased both the content of soil particles with the diameter lesser than 0.02 mm and the quantity of molybdenum forms. Plants cultivated

Table 4. Yield (t/ha) and molybdenum (Mo) uptake (g/ha) by selected plants and content of Mo in soil

Plant	Yield			Molybdenum uptake		
	minimum	maximum	average	minimum	maximum	average
Winter wheat (*Triticum aestivum*)	3.20	7.20	4.13	2.24	5.04	2.89
Rye (*Secale cereale*)	2.30	5.80	2.40	1.61	4.06	1.68
Green forage corn (*Zea mays*)	30.00	58.00	48.00	4.50	8.70	7.20
Winter rape (*Brassica napus*)	2.20	4.00	2.24	2.20	4.00	2.66
Potato (*Solanum tuberosum*)	12.00	45.00	23.20	1.32	4.95	2.55
Sugar beet (*Beta vulgaris*)	15.00	69.00	57.40	2.55	11.73	9.76

Mo quantity in the solution of soil arable layer					
Minimum	maximum	average	minimum	maximum	average
	(μmol/L)			(g/ha)	
0.0021	0.091	0.027	0.19	8.25	2.45

*according to the Concise Statistical Yearbook of Poland (2016) and Jadczyszyn (2000)

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in sandy, acidic soils may show deficiencies of Mo due to the low molybdenum concentration in soil solution as well as soil characteristics that limit its availability to the plants. Regular liming of soils and fertilization with phosphorus can improve the availability of molybdenum to plants.

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