Influence of gypsum treatment on extractability of nutrients from soils

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ABSTRACT

In an incubation experiment with 36 soils we tested the influence of application of 3.3 g of $CaSO_4.2\ H_2O$ per kg of soil on extractability of nutrients (P, K, Mg, Ca, Mn, B and S). After 134-day incubation of gypsum-treated soils the soils were extracted with water (1:5, w/v), 0.5M ammonium acetate with NH_4F addition (pH 7) and by Mehlich 3 method. An ICP-technique was used for nutrient detection and colorimetry on a SKALAR analyser was employed to determine phosphates and sulphates. The most interesting results were measured in phosphorus. P concentration was markedly lower in the H_2O extract after gypsum treatment, on average by 69% in ICP detection and by 58% in colorimetric detection of phosphates. A significant depression of P concentration was also measured in the acetate extract, but it was considerably lower (11% in ICP detection, 14% in colorimetry). On the contrary, in Mehlich 3 extraction the concentration after gypsum treatment was higher on average by 31% in ICP detection while colorimetry detection did not show any significant differences. The results indicate that it is necessary to identify the method of soil extraction including the method of analytical determination of the nutrient, when the nutrient status of soils is to be evaluated.

Keywords: gypsum treatment of soils; soil tests; phosphorus; potassium; magnesium; calcium; manganese; boron; sulphur

In last decennium atmospheric depositions of sulphur in the Czech Republic were an important source of sulphur for soils that masked the negative balance of sulphur input to soils through fertilisation in form of so called ballast-free fertilisers. For example, atmospheric depositions in 1992 amounted nearly to 100 kg S/ha but currently they are not higher than 10 kg S/ha. Air quality improved radically as a result of reductions in sulphur dioxide emissions from brown coal burning mainly in the power-engineering sector – in thermal power plants. A by-product of desulphurisation of gases from the burning of fossil fuels is so called energy gypsum that is now a valuable raw material for the manufacture of plasterboards for the building industry and could be used to diminish sulphur deficiency in agriculture on a larger scale.

According to our monitoring, on average only a third of arable lands in the Czech Republic had a sufficient reserve of labile sulphur for the last four years. Therefore, it is not surprising that sulphur deficiency is often indicated in crops with high requirements for sulphur nutrition such as rape.

Our studies of sulphur behaviour in soils of Czech Republic demonstrated an intensive sulphur immobilisation after applications of sulphur in form of ammonium sulphate in most examined soils (Matula et al. 2000). Deficient sites have lighter permeable soils with percolative regimes. The low water solubility of gypsum should be a positive feature in percolative S-deficient soils. It should be a more stable source of inorganic sulphur for nutrition. At a single application of higher doses, gypsum should perform the function of a slow-acting fertiliser, gradually release sulphates for plants; it should be a safer source for crop nutrition than sulphur mobilisation from mineralization of soil organic matter. A potential contribution of sulphur from soil organic matter to crop nutrition is practically insignificant. Eriksen (1994) stated that a possible supply of plant-available sulphur from 1 gram of soil per year was in the range of 3–7 μg S. Gypsum treatment of soils is an old fertilisation practice, used especially to ameliorate alkaline salinised soils. Positive impacts of gypsum treatment on the health of crops were also reported by Allmars et al. (1987).

The objective of our experiment was to determine the effect of a single gypsum dose (about 2 t Ca/ha) on the nutrient status of agricultural soils in the Czech Republic and to describe potential changes in the nutrient supply of soil by multinutrient soil tests. Based on previous studies of preventive diagnostics of the nutrient status of soils by multinu-

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trient soil tests (Matula 1999a, b) three tests were chosen from the set of soil tests: water extraction at a 1:1 ratio, extraction with 0.5M ammonium acetate with addition of ammonium fluoride and Mehlich 3 extraction – an official procedure of soil testing in the Czech Republic.

MATERIAL AND METHODS

To establish the incubation, experiment soil samples were taken from the topsoil profile on 36 farmed plots in 22 different localities in the Czech Republic. The soil samples were air-dried, homogenised by screening through a 2-mm sieve and dosed by 50 g into incubation pots 150 ml in volume. Table 1 shows succinct information on the used soils. Two variants were established for each soil: a control variant and a response variant, in triple replication each. An amount of 0.165 g $CaSO_4.2\,H_2O$ was admixed into 50 g of soils of the response variant and soil in all incubation pots were moistened with distilled water to provide 70% maximum moisture capacity. The specification of input irrigation for particular soils was derived from a regression equation with the value of cation exchange capacity of soils (Matula et al. 2000). The incubation experiment lasted 134 days under a daily temperature regime: 16 hours 20°C, 8 hours 15°C. During the experiment the soil moisture in incubation pots was maintained by weighing off distilled water to the initial value.

After 134 days of incubation soils were extracted by three different methods: water extraction at a 1:5 ratio (w/v) (SPAC 1999); 0.5M ammonium acetate extraction with addition of ammonium fluoride of pH 7 (Matula 1996); and Mehlich 3 extraction (SPAC 1999). These nutrients were determined in the extracts: K, Mg, Ca, Mn, P and S using an ICP-OES Trace Scan analyser (Thermo Jarrell Ash). In all three types of extracts phosphates were determined by colorimetry of the reduced phospho-molybdate blue complex on a San Plus SKALAR System analyser. A SKALAR analyser was also used to determine sulphates in the water extract.

The programme GraphPad PRISM, Ca., USA, version 3, was used for statistical processing of experimental results.

RESULTS AND DISCUSSION

Phosphorus

Tables 2 and 3 show the summarisation and statistical evaluation of results of phosphorus extraction by three multinutrient tests after 134 days of incubation experiment.

In the water extract of soils with gypsum treatment was measured a markedly lower concentration of water-soluble phosphorus (Figures 1 and 2). Compared to the control variant (i.e. without gypsum) the phosphorus concentration was lower by 69% on average if detected by the ICP technique and by 58% at colorimetric detection of phosphates on the SKALAR analyser.

If 0.5M ammonium acetate extraction of soils with addition of ammonium fluoride was used, the concentrations of phosphorus extracted from soils after gypsum treatment were also significantly lower (Tables 2 and 3), but differences from the control variant were considerably smaller. Detection of extractable phosphorus on the ICP analyser indicated the values lower by 11% on average and detection of phosphates on the SKALAR analyser by 14% lower.

Mehlich 3 extraction of soils provided quite a different situation (Tables 2 and 3). Firstly, all measured values were considerably higher than in the preceding extraction methods. Secondly, higher concentrations of extractable phosphorus detected by the ICP technique were determined in the gypsum treatment, on average by 31% higher than in the control variant. No statistically significant differences between the sets of soils of control and response (gypsum)

Table 1. Information about the nutrient status of the experimental set of soils

Statistics	pH 0.2M KCl (1:1, w/v)	CEC (mmol/kg) (Matula 1996)	C_{ox} (%) (Sims and Haby 1971)	Soil test: water extraction (1:5, w/v) (SPAC 1999)						
				K	Mg	Ca	Mn	P	S	B
				mg/kg (determined by ICP)						
Minimum	4.08	95	1.20	8.20	4.00	39.6	0.133	1.19	8.17	0.078
Median	5.76	125	1.94	30.55	15.65	91.65	0.547	4.21	13.81	0.162
Maximum	6.94	256	2.89	183.20	64.20	200.60	1.431	15.98	36.92	0.797
Mean	5.75	133	1.96	38.56	18.14	106.1	0.588	5.63	16.24	0.191
CV%	11.46	24.8	20.6	31.47	57.01	97.91	51.57	55.8	38.59	66.83

Table 2. Influence of gypsum treatment on extractable phosphorus from soils determined by ICP-technique

Statistics	Soil extraction – soil test (mg P/kg)					
	water		ammonium acetate		Mehlich 3	
	control	treated	control	treated	control	treated
Minimum	1.190	0.110	3.2	2.3	41	47
Median	4.205	1.435	17.15	16.05	135.5	160.0
Maximum	15.98	7.08	57.80	46.90	368	412
CV%	55.80	86.54	60.09	55.58	54.99	51.46
Paired *t*-test, two-tailed, number of pairs = 36						
P-value	< 0.0001		< 0.0001		< 0.0001	
Are means significantly different? ($P < 0.05$)	yes		yes		yes	
Mean of differences	3.724		2.372		–40.64	
95% confidence interval	3.030–4.419		1.400–3.345		(–51.99)–(–29.28)	
R^2	0.7721		0.4123		0.6016	

variant were proved by the colorimetric detection of phosphates on the SKALAR analyser.

The aim of soil tests is to provide information on the nutrient status of soils in order to rationalise fertilisation of soils and crops. The soil test should capture the source of nutrients in the most effective way so that it would be as consistent as possible with the real source of plant nutrition at a site (on a plot, in a substrate…). The term available nutrients is normally used for nutrients extracted by soil tests. As documented by the above results, we obtained contradictory results in phosphorus in our experiment, especially between the method of water extraction of soils and Mehlich 3 method. We detected a marked depression of phosphorus concentration after gypsum treatment in the water extract but an increase in phosphorus extraction by Mehlich 3 method detected on the ICP analyser. The results indicate that the general usage of the term available phosphorus is not correct for different soil tests. The general usage of the term available nutrients without specifying the method of acquiring the data must then lead to problems with an agronomic interpretation of soil test results.

Table 3. Influence of gypsum treatment on extractable phosphates from soils determined by SKALAR flow analyser (colorimetry of phospho-molybdate blue complex)

Statistics	Soil extraction – soil test (mg P/kg)					
	water		ammonium acetate		Mehlich 3	
	control	treated	control	treated	control	treated
Minimum	0.41	0.02	1.7	1.6	14.0	40.0
Median	3.255	1.345	16.85	15.90	112.0	120.5
Maximum	11.58	6.89	60.5	46.4	346	351
CV%	71.59	89.48	63.68	59.07	60.39	55.93
Paired *t*-test, two-tailed, number of pairs = 36						
P value	< 0.0001		< 0.0001		0.1765	
Are means significantly different? ($P < 0.05$)	yes		yes		no	
Mean of differences	2.178		2.964		–5.222	
95% confidence interval	1.673–2.682		1.942–3.986		(–12.91)–2.468	
R^2	0.6871		0.4979		0.0516	

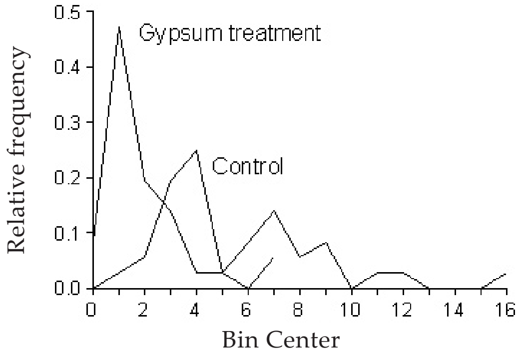

Figure 1. Frequency distribution of phosphorus concentrations in the water extract of soils, determined by ICP-technique

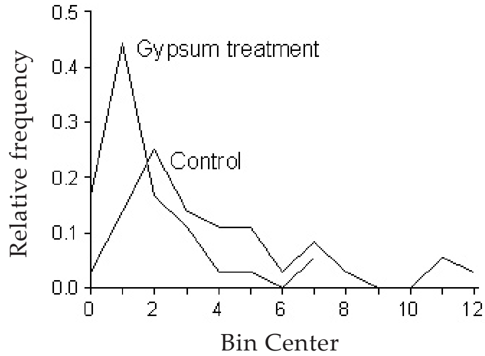

Figure 2. Frequency distribution of phosphate concentrations in the water extracts of soils determined by colorimetry of the phospho-molybdate blue complex

To explain the contradictory results of water extraction and Mehlich 3 method we do not have any information on the consistency of the values determined by soil tests with phosphorus bioavailability. In the paper by Matula (2004), in a collection of 48 different soils we similarly determined a significant depression of phosphorus uptake and concentration in young barley plants in the variant of sulphur fertilisation where ammonium sulphate was applied. This finding could indirectly support the assumption that water extraction of phosphorus from soils should reflect real bioavailability of phosphorus more consistently than Mehlich 3 extraction that indicated a higher concentration of extractable phosphorus in the sulphate variant.

If the nutrient status of soils is tested for phosphorus, the results of our experiment also show that it is necessary to indicate the method of analytical determination of phosphorus in the extract besides the method used for phosphorus extraction from the soil (i.e. soil test identification). Otherwise, the values of soil tests might be misunderstood or misinterpreted from agronomic aspects. Previously reported values of tests of phosphorus reserves in soils were mostly the results of colorimetric determination of inorganic phosphate by colorimetry of the reduced phospho-molybdate blue complex.

Nowadays, when the ICP technique has been introduced into routine soil tests, we can speak about completely different values because total

Table 4. Statistics of phosphorus detection by ICP-technique and colorimetry in soil extracts

	Water 1:5 (mg P/kg)				NH_4-acetate (mg P/kg)				Mehlich 3 (mg P/kg)			
	control variant		treated variant		control variant		treated variant		control variant		treated variant	
	ICP	SKALAR	ICP	SKALAR	ICP	SKALAR	ICP	SKALAR	ICP	SKALAR	ICP	SKALAR
Minimum	1.19	0.41	0.11	0.02	3.2	1.7	2.3	1.6	41	37	47	40
Median	4.205	3.255	1.435	1.345	17.15	16.85	16.05	15.40	135.5	116.5	160.0	120.5
Maximum	15.98	11.58	7.08	6.89	57.8	60.5	46.9	46.40	368	346	412	351
CV%	55.8	71.6	86.5	89.5	60.1	63.7	55.9	59.2	55.0	59.9	51.5	55.9
Paired *t*-test, two-tailed, number of pairs = 36												
P-value	< 0.0001		< 0.0001		0.301		< 0.0001		< 0.0001		< 0.0001	
Significance ($P < 0.05$)	yes		yes		no		yes		yes		yes	
Mean of differences	1.633		0.0875		0.1917		0.8111		12.47		51.42	
95% confidence interval	1.376–1.890		0.04975–0.1252		(–0.1793)–0.5626		0.5591–1.063		9.204–15.74		39.35–63.49	
R^2	0.8264		0.9978		0.0305		0.5498		0.6320		0.6815	

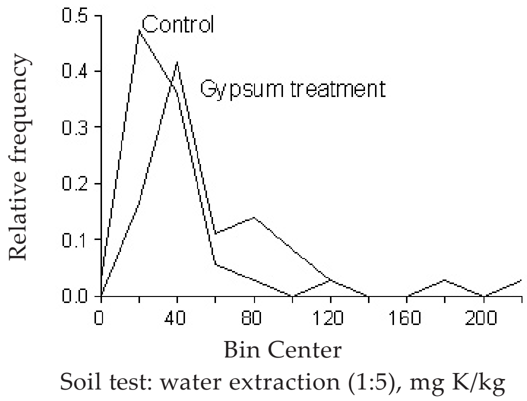

Figure 3. Frequency distribution of potassium concentrations in the water extract of soils

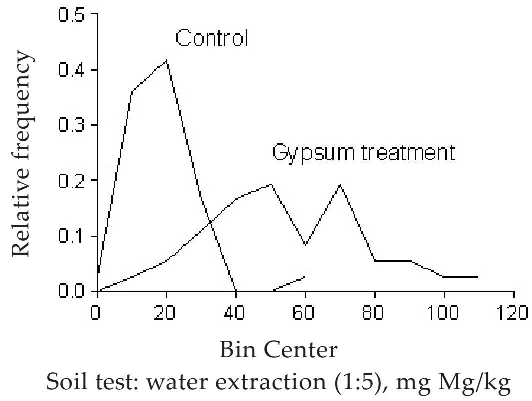

Figure 4. Frequency distribution of magnesium concentrations in the water extract of soils

phosphorus is determined, which may comprise a high proportion of the extractable fraction of organic phosphorus besides inorganic phosphorus. This problem is demonstrated and statistically evaluated in Table 4.

Potassium

As expected, a marked increase in potassium concentration was measured only in the water extract in most soils after gypsum treatment (Figure 3). Potassium concentration was higher by 62% on average than in the control. It can be explained by the establishment of equilibriums between cations of the solid and liquid phase of soils after the input of calcium into the environment from applied gypsum.

In the ammonium acetate extraction the paired *t*-test indicates significant differences between control variant and gypsum treatment. However, the differences in absolute values of soluble and exchangeable potassium were practically negligible. No statistically significant differences were found out by Mehlich 3 extraction.

Magnesium

Similarly, the differences in magnesium concentration between control variant and gypsum treatment in the water extract were influenced by the establishment of equilibriums between the liquid and solid phase after the input of calcium from gypsum (Figure 4). Differences in the relations were bigger than in the case of potassium. Mg concentration in the water extract was approximately three times higher than in the control variant. In the other soil tests (ammonium acetate and Mehlich 3) that also capture the exchangeable fraction Mg^{2+} the differences between control variant and gypsum treatment were not so large although the paired *t*-test indicated significantly lower values of extractable magnesium after gypsum treatment.

Calcium

Changes in calcium concentrations in soil extracts after gypsum treatment are shown in Figures 5–7. In water extraction of soils there was logically an extreme increase in extractable calcium after gypsum treatment. The ammonium acetate extraction did not indicate any noticeable differences between the experimental variants even though the differences were statistically significant. In this case the results could be influenced by the addition of ammonium fluoride that causes calcium precipitation to form the insoluble compound calcium fluoride. On the contrary, remarkably higher values of calcium were detected after gypsum treatment in Mehlich 3 extract. It shows that Mehlich 3 agent was aggressive against calcium sulphate that is otherwise a little soluble compound.

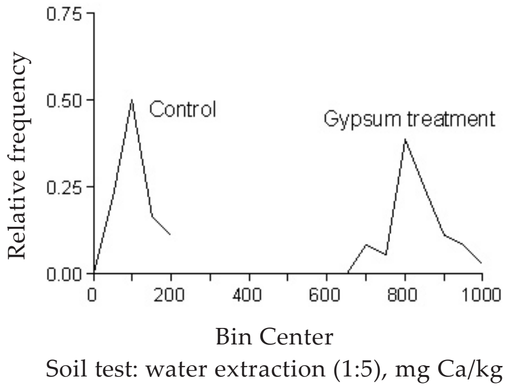

Figure 5. Frequency distribution of calcium concentrations in the water extract of soils

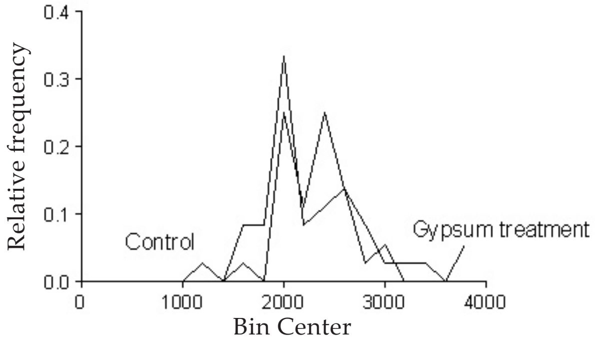

Figure 6. Frequency distribution of calcium concentrations in the ammonium acetate extract (with addition of ammonium fluoride) of soils

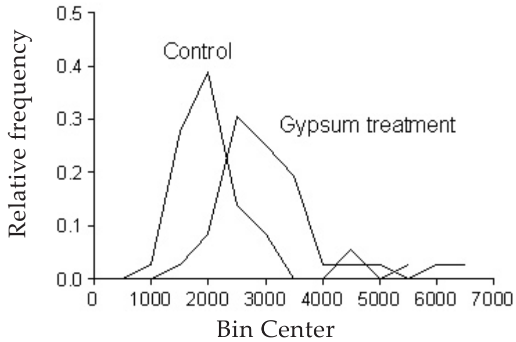

Figure 7. Frequency distribution of calcium concentrations in Mehlich 3 extract of soils

Manganese

Table 5 shows the effects of gypsum treatment of soils on manganese concentration in soil extracts. A depression of manganese concentration in the water extract by 40% on average was found out in most soils after gypsum treatment. The paired *t*-test proved significant differences between the set of control soils and the gypsum treatment only in water extraction of soils. High values of manganese concentration in the Mehlich 3 extract, compared to the other used extractions, are in agreement with the acid nature of the agent that enables to transform insoluble forms of manganese into soluble Mn^{2+}. Hence, these values of the soil test do not correspond to plant bioavailability of manganese (Matula 1999a).

Boron

All three extraction methods showed an important influence of gypsum treatment on boron extraction. In water extraction and Mehlich 3 method boron concentration in the extract decreased after gypsum treatment while it increased in the ammonium acetate extraction. Nevertheless it cannot be established from the given experiment which result of the soil test will be more consistent with plant boron availability.

Sulphur

Gypsum treatment increased sulphur concentrations in all three types of soil extraction. Table 6

Table 5. Influence of gypsum treatment on extractable manganese from soils

Statistics	Soil extraction – soil test (mg Mn/kg)					
	water		ammonium acetate		Mehlich 3	
	control	treated	control	treated	control	treated
Minimum	0.133	0.004	1.060	0.830	39	39
Median	0.547	0.088	2.70	2.52	96	96
Maximum	1.431	2.70	11.93	22.8	198	174
CV%	51.57	230.78	60.54	116.32	36.39	32.10
Paired *t*-test, two-tailed, number of pairs = 36						
P-value	0.0019		0.7787		0.0568	
Are means significantly different? ($P < 0.05$)	yes		no		no	
Mean of differences	0.324		–0.0942		2.306	
95% confidence interval	0.1285–0.5195		(–0.7696)–0.5813		(–0.0719)–4.683	
R^2	0.2446		0.0023		0.09982	

Table 6. Statistics of sulphur detection in the water extract from soils by ICP-technique and colorimetry of sulphates by the methylthymol blue method

Statistics	Soil extraction: water (mg S/kg)			
	control variant		treated variant	
	ICP	SKALAR	ICP	SKALAR
Minimum	8.17	3.71	653	358
Median	13.81	7.105	707.5	393
Maximum	36.92	16.19	769	472
CV%	38.59	38.07	3.95	5.11
Paired *t*-test, two-tailed, number of pairs = 36				
P value	< 0.0001		< 0.0001	
Are means significantly different? ($P < 0.05$)	yes		yes	
Mean of differences	8.409		312.7	
95% confidence interval	7.105–9.714		303.9–321.6	
R^2	0.8305		0.9933	

shows a comparison of sulphur concentrations in the water extract determined by different terminal analyses: total sulphur by the ICP technique and sulphates on the SKALAR analyser. Considerably higher values of sulphur content detected on the ICP analyser, compared to sulphates measured on the SKALAR analyser, could indicate a possibility of huge transformation, immobilisation of sulphates into organic forms. In our previous paper dealing with sulphur in the soil (Matula et al. 2000) we observed sulphur applications in form of ammonium sulphate; in a set of 45 different soils the supplied mineral sulphur interfered with total content of soil organic matter sulphur and labile forms of sulphur were immediately involved in transformations of soil organic matter. A possibility of fast and significant involvement of labile sulphur in free organic components of soil was reported by Eriksen (1997).

pH and nitrates

The paired *t*-test indicated significant differences in the measured pH values (0.2M KCl) between the control variant and gypsum treatment. The differences were however not so important from the practical aspect of absolute values. Changes in nitrate concentrations in the water extract were specific in each particular soil. A marked increase in nitrate content was found out in 18 out of 36 soils; on average, it exceeded an opposite trend in the second half of the set of soils.

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ABSTRAKT

Vliv síranu vápenatého na extrahovatelnost živin z půdy

V inkubačním pokusu se 36 půdami byl ověřován vliv aplikace 3,3 g $CaSO_4.2\ H_2O$/kg (SV) půdy na extrahovatelnost živin (P, K, Mg, Ca, Mn, B a S). Po 134 dnech inkubace půd se SV byly půdy extrahovány vodou (1 : 5; w/v), 0,5M octanem amonným s přídavkem NH_4F (pH 7) a postupem Mehlich 3. K detekci živin byla použita ICP-technika a pro stanovení fosfátů a síranů kolorimetrie na analyzátoru SKALAR. Nejzajímavější výsledky byly zjištěny u fosforu. V H_2O-extraktu půd po aplikaci SV byla výrazně nižší koncentrace P, v průměru o 69 % při ICP-detekci a o 58 % při kolorimetrické detekci fosfátů. Rovněž v acetátovém extraktu došlo k průkazné depresi koncentrace P, ale podstatně menší (11 % ICP-detekce, 14 % kolorimetrie). Naopak u extrakce Mehlich 3 byla po aplikaci SV koncentrace P v průměru větší o 31 % při ICP-detekci, zatímco při kolorimetrickém stanovení nebyly rozdíly průkazné. Z výsledků je zřejmé, že při posuzování výživného stavu půd je třeba uvádět metodu extrakce půdy včetně způsobu analytického stanovení živiny.

Klíčová slova: sádrování půd; půdní testy; fosfor; draslík; hořčík; vápník; mangan; bór; síra

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