A relationship between multi-nutrient soil tests (Mehlich 3, ammonium acetate, and water extraction) and bioavailability of nutrients from soils for barley

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ABSTRACT

The aim of the paper was to test the universality of three multi-nutrient soil tests after a radical intervention in soil chemistry by gypsum treatment on a variable set of 36 soils. Pot experiments with barley in a growth chamber were conducted to determine the bioavailability of K, Mg, P, Mn and B from soils. There were no marked differences in correlations between soil tests and the plant in K, Mg and P. But in the case of Mn and B Mehlich 3 test was not in appropriate agreement with the plant. Shortcoming of water extraction is missing information of capacity character for the derivation of the fertilizer recommendations on heterogeneous soils. The highest universality of NH_4-acetate soil test was proved in all studied nutrients (K, Mg, P, Mn, B) in relation to the plant. Determination of the CEC value that extends the information of capacity character is a part of this soil test. The CEC value contributes to a more sophisticated approach to interpretation for the fertilizer recommendations.

Keywords: soil testing; Mehlich 3; ammonium acetate extraction; water extraction; bio-availability; potassium; magnesium; phosphorus; manganese; boron

Regardless of their present drawbacks chemical methods of agricultural soil testing are the most frequently used tools of diagnostics of the nutrient status of soil and the need of fertilisation derived from it. The main advantage of soil tests is a possibility of preventing potential disorders of the nutrient status of the crop before its own cultivation in a given field. Raij (1998) considered soil testing as a remarkable and unique activity that synthesises a large amount of research information and scientific knowledge for practical needs of the identification and prevention of the majority of disproportions in plant nutrition. Soil testing provides farmers with the highest quantity of practically applicable information.

Today's challenge (Peck and Soltanpour 1990, Houba et al. 1994, Jones 1998) is to select from the collection of soil extraction tests such methods that allow simultaneous extraction of several nutrients so that it will be possible to make full use of the advantages of multi-element analysers, e.g. ICP. A crucial condition is that the soil test will identify a similar source of nutrients that will really be available to plants (Peck and Soltanpour 1990, Raij 1998).

The majority of the present methods of soil tests date back to the period after World War I, i.e. to the beginnings of more intensive use of commercial fertilisers when the sensitivity of analytical methods was lower. This drawback was compensated by a higher strength of nutrient extraction from the soil that has been handed down until now e.g. in Mehlich 3 extraction used in this country.

After the intensity of application of commercial fertilisers of NPK type has increased, it is necessary to have more detailed information on the storage rate and complex of all nutrients including trace elements in the soil. There is also an increasing need for more exact determination of nutrient availability to plants in a wide range from deficiency through optimum to excess and their mutual relations and interactions. Such a specification is essential for the needs of fully effective management of nutrient inputs (economic aspect) and indispensable load of soil (ecological aspect). The improvement and precision of diagnostic methods

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Funding for this research was provided by the Ministry of Agriculture of the Czech Republic, Grant No. QH82281.

of the nutrient status of soils is an instrument significantly contributing to the improvement of technologies of better utilisation of plant nutrients for the formation of yields of agricultural crops with high-quality parameters and without harmful impacts on the environment at the same time.

Requirements for a modern method of soil test can be summarised in the following seven items (Skogley 1994, Raij 1994): (1) Simultaneous extraction of all important nutrients from the soil (so called multinutrient test). (2) Functionality in all kinds and types of soils, i.e. existence of the best possible compliance of extracted nutrients from heterogeneous soils with their real bioavailability – requirement of universality. (3) Accuracy – reproducibility. (4) Simplicity. (5) Reasonable price in agreement with the utility value of information. (6) Expeditious detection. (7) Reflection of mechanisms (parameters) influencing the availability of a nutrient to plants from the soil in a given site – field. Of course, none of the present methods of soil testing fulfils these ideal parameters. But the suitability of methods can be evaluated by considering how they approximate the above-mentioned criteria.

Many authors (Raij 1994, Skogley 1994, etc.) believe that soil tests may be improved by the use of ion-exchange resins that can simulate the mechanism of nutrient transport to roots – to the sink. But the methods using ion-exchange resins are more labour and time consuming. In our study (Matula 1999), where we compared 6 extraction methods with ion-exchanger capsules, the assumed advantages of ion-exchanger method compared to traditional extraction methods were not proved from the aspect of correlation with bioavailability of nutrients (K, P, Mg, Mn, S).

Correlations between the values of soil test and bioavailability of nutrients are an essential condition for the substantiation of further calibration research for the needs of agronomic interpretation of soil test. To prove the advantages of a soil test in field conditions is a long and costly process because of the impact of variable and hardly controllable factors of the site and years. The fastest method of correlation research is pot experiments with a larger set of different soils under controlled cultivation conditions of the growing of a test plant when the impact of uncontrollable variables may be eliminated (Dahnke and Olson 1990).

In the soil–plant system (Figure 1) the value of cation exchange capacity (CEC) of soil plays a dominant role in the establishment of equilibriums between soil solution and solid phase of soil. The CEC value takes up an important integration position in the whole soil – plant system, enabling a more sophisticated approach in the first phases of the calibration process of agronomic interpretation of soil tests for the needs of fertilisation rationalisation. From this aspect, the CEC value is a part of NH_4-acetate soil test (Matula 1996).

The objective of our study was to verify the universality of three multinutrient tests after a radical intervention in soil chemistry by gypsum treatment

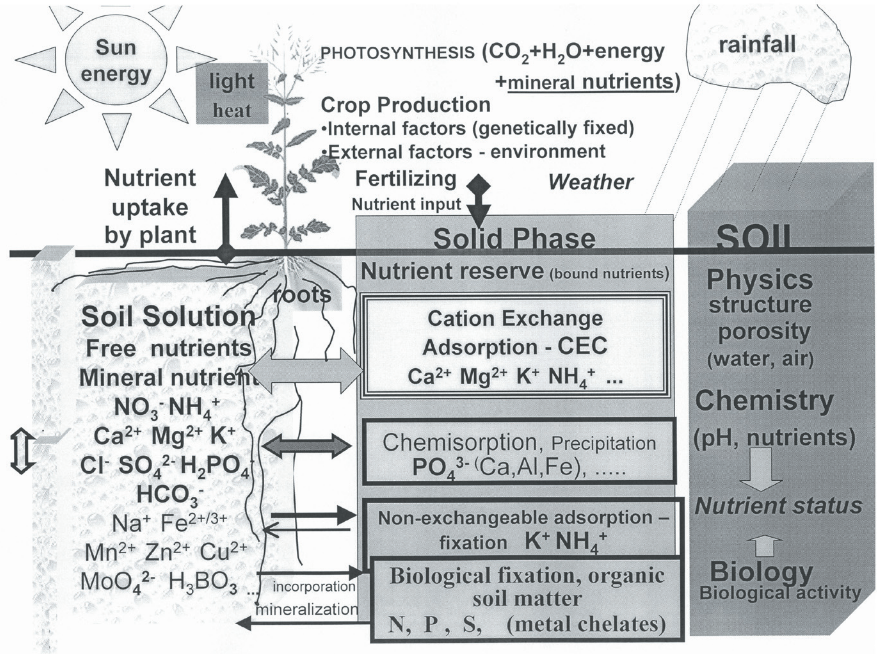

Figure 1. Schema of soil-plant system

in a heterogeneous set of 36 soils by means of correlations between soil tests and bioavailability of main nutrients (K, Mg, P) and trace elements (Mn and B).

MATERIAL AND METHODS

Thirty-six soils from top soils of agriculturally farmed fields in 22 localities of the Czech Republic were used for the study. Bulk samples of soil were air-dried and homogenised by screening through a 2-mm sieve. The basic set of 36 soils was doubled when the same soil samples with gypsum addition at an equivalent dose of 2 t Ca per hectare were used. The purpose was to verify the universality of soil test information about potassium, magnesium, phosphorus, manganese, and boron after a radical intervention in soil chemistry by gypsum treatment. Tables 1, 2, and 3 show some agrochemical characteristics of the set of used soils. Three soil tests were employed to evaluate the nutrient status of soils: Mehlich 3 (Zbíral 2002), water extraction of soils at a 1:5 ratio w/v (SPAC, 1999) and extraction with 0.5M ammonium acetate with addition of ammonium fluoride (Matula 1996). The ICP-OES technique on a Thermo Jarrell Ash Trace Scan Analyser was used to detect the nutrients in extracts.

The whole set ($n = 72$) was studied for biologically available nutrients on barley as the test crop. The method of testing biological availability was similar to that in Matula (2004). Short-term (21-day) pot trials were established on each soil with spring barley cv. Akcent as a test plant using this scheme: C – control variant, without gypsum application; T – treated (response) variant, with the application of 0.33 g $CaSO_4 \cdot 2H_2O$ (gypsum) per 100 g of soil. Each variant had three replications. Vegetation pots with 6 cm in diameter were filled with 100 g of soil that was mixed with 80 g of coarse-grained quartz sand.

Fifteen barley seeds (after their washing and one-hour soaking in distilled water) were planted onto the soil-sand mixture surface in vegetation pots and covered with 25 ml of coarse-grained quartz sand. The moistening of vegetation pots was differentiated on the basis of an experimentally determined relationship between the field water capacity of soil and the value of its cation exchange capacity (CEC) (Matula et al. 2000). The moisture content was regularly renewed according to the weight loss of vegetation pot.

Cultivation took place in a plant growth chamber with the light and temperature regime: daylight 16 h, 20°C, dark 8 h, 15°C; photosynthetically active radiation 500 $\mu E/m^2/s$. Nitrogen dose of 6 mg N/pot, as a solution of NH_4NO_3, was applied jointly with watering on days 3, 7, 11, 14 and 17 since the trial establishment. Harvested barley shoots were instantly dried at 65°C.

A Milestone microwave device was used for mineralization of barley dry matter in the medium of nitric acid and hydrogen peroxide; the analysis was carried out on an ICP-OES Trace SCAN apparatus (Thermo Jarrell Ash).

Statistical programme GraphPad PRISM, Ca., USA, version 3.0, and Microsoft Excel 2000 were used to evaluate the experimental results.

RESULTS AND DISCUSSION

Calcium and sulphur were excluded from the studies of correlations between nutrients in soil and in plant because the gypsum application markedly changed the range of their concentrations in extracts (Tables 1–3). The measured values of calcium and sulphur concentrations in the whole set of soils ($n = 72$) did not satisfy the condition for the use of correlation analysis, i.e. Gaussian distribution.

Table 4 shows the calculated coefficients of correlation (r) between soil tests and studied nutrients in plant.

Potassium. The closest correlations between soil tests and plant were found in potassium. The values of correlation coefficients were similar in all three soil tests (Table 4). The transformation of potassium concentration in soil extracts to the activity ratio ($K/\sqrt{Ca + Mg}$) according to Beckett (1964) improved the closeness of correlations with plant only in NH_4-acetate extraction and in Mehlich method, i.e. in soil tests that register water-soluble and exchangeable potassium, providing information on the capacity reserve of easily available potassium to plants. Similar improvement of the correlation between soil and plant was observed when the simplified activity ratio ($K/\sqrt{Ca}$) according to Wild (1988) was used (Table 5). In the soil test with NH_4-acetate extraction, where the determination of CEC value is its part, the expression of potassium reserve as the percentage of potassium equivalents in the CEC value did not improve the closeness of the correlation with potassium in plant.

Table 1. Information about the nutrient status of the experimental set of soils detected in water extractant (1:5; w/v)

Set of soils	Statistics	K	Mg	Ca	P	S	Mn	B
		mg/kg (determined by ICP)						
n = 72 Control Gypsum	minimum	8.20	4.00	39.60	0.11	8.17	0.004	0.072
	median	36.85	26.65	441.80	3.06	345.00	0.310	0.139
	maximum	212.10	110.8	1024.00	15.98	769.00	12.010	0.797
	coef. var. %	79	70	79	83	96	258	61
n = 36 Control	minimum	8.20	4.00	39.60	1.19	8.17	0.133	0.078
	median	30.55	15.65	91.65	4.21	13.81	0.547	0.162
	maximum	183.20	64.20	200.60	15.98	36.92	1.431	0.797
	coef. var. %	85	57	40	56	39	52	67
n = 36 Gypsum	minimum	12.30	7.90	683.00	0.11	653.00	0.004	0.072
	median	47.05	51.30	822.30	1.44	707.5	0.088	0.125
	maximum	212.10	110.80	1024.00	7.08	769.00	12.010	0.319
	coef. var. %	49	41	8	87	4	386	37

Magnesium. Compared to potassium, low correlations of soil tests with magnesium in plant were calculated (Table 4).

In general, there exist marked interactions of antagonistic character in the uptake of cations by plant where potassium takes up a dominant position (Mengel and Kirkby 1982). To define an appropriate storage rate of magnesium in soil preceding optimisation of potassium reserve in soil is necessary (Matula et al. 1996).

The transformation of measured magnesium concentrations in soil extracts to the ratio to potassium (Mg/K) considerably improved the closeness of correlations with magnesium in plant (Table 6), which confirms a significant role of potassium in soil to achieve the good-quality mineral composition of vegetative biomass, mainly of forages and leaf vegetables (Grunes 1983, Grunes and Welch 1989). The expression of magnesium reserve in soil as the percentage of magnesium equivalents

Table 2. Information about the nutrient status of the experimental set of soils detected in NH_4^-acetate extractant

Set of soils	Statistics	C_{ox} (Sims, Haby 1971)	pH 0.2M KCl (1:1; w/v)	CEC (mmol/kg)	K	Mg	Ca	P	S	Mn	B
					mg/kg (determined by ICP)						
n = 72 Control Gypsum	minimum	1.20	4.08	90	82	22	1229	2.3	3.7	0.83	0.010
	median	1.92	5.75	125	177	104	2286	16.6	323.7	2.59	0.135
	maximum	2.89	6.99	256	831	430	3878	57.8	848	22.80	0.700
	coef. var. %	20	11	25	63	57	23	58	98	93	72
n = 36 Control	minimum	1.20	4.08	95	82	22	1229	3.2	3.7	1.06	0.010
	median	1.94	5.76	125	176	106	2030	17	12	2.71	0.125
	maximum	2.89	6.94	256	821	430	3804	57.8	29	11.93	0.700
	coef. var. %	21	11	25	64	56	24	60	52	61	78
n = 36 Gypsum	minimum	1.22	4.17	90	83	24	1695	2.3	618	0.83	0.505
	median	1.91	5.71	123	180	104	2350	16.1	689	2.52	0.145
	maximum	2.69	6.99	252	831	423	3878	46.9	848	22.80	0.690
	coef. var. %	19	11	25	63	57	20	56	8	116	67

Table 3. Information about the nutrient status of the experimental set of soils detected in Mehlich 3 extractant

Set of soils	Statistics	K	Mg	Ca	P	S	Mn	B
		mg/kg (determined by ICP)						
n = 72 Control Gypsum	minimum	89	55	942	41	16	39	0.08
	median	218	155	2424	141	347	96	0.17
	maximum	1032	475	6581	412	2139	412	0.33
	coef. var. %	60	48	40	54	104	34	28
n = 36 Control	minimum	89	73	942	41	16	39	0.11
	median	223	163	1981	136	24	96	0.20
	maximum	1032	475	5463	368	61	198	0.33
	coef. var. %	61	48	42	55	35	36	26
n = 36 Gypsum	minimum	94	55	1608	47	632	39	0.08
	median	211	151	2944	160	790	96	0.16
	maximum	910	458	6581	412	2139	174	0.31
	coef. var. %	59	48	33	51	32	32	30

in the CEC value improved the closeness of correlation with magnesium in plant.

Phosphorus. Using the soil tests, largely different values of phosphorus were extracted from soils (Tables 1–3). The method of analytical determination of phosphorus also influenced phosphorus concentrations in extracts (Table 8). If the result of phosphorus reserve determination in soil is given, besides the soil test it is also necessary to indicate the method of analytical determination

Table 4. Correlation between soil tests and nutrients in shoots of barley

Nutrient	Soil test (extractant)	Correlation coefficient (*r*)	
		concentration in barley	nutrient uptake
Potassium	water	0.7146	0.8151
	NH_4-acetate	0.7498	0.8260
	Mehlich 3	0.7559	0.7901
Magnesium	water	0.4630	0.7401
	NH_4-acetate	0.3778	0.4644
	Mehlich 3	0.4864	0.3948
Phosphorus	water	0.8171	0.8105
	NH_4-acetate	0.4727	0.6463
	Mehlich 3	0.4498	0.6042
Manganese	water	0.6932	0.6870
	NH_4-acetate	0.6607	0.6870
	Mehlich 3	0.0065	-0.0393
Boron	water	0.5868	0.5929
	NH_4-acetate	0.6707	0.6821
	NH_4-acetate (corrected)	0.7394	0.7602
	Mehlich 3	0.1218	0.1227

Table 5. Correlation between adjusted K-characteristics of soil tests and nutrients in barley shoots

Potassium value transformation	Soil test (extractant)	Correlation coefficient (*r*)	
		K-concentration in barley	K-uptake
K/√Ca + Mg	water	0.6387	0.6338
K/√Ca		0.6154	0.6053
K/√Ca + Mg	NH$_4$-acetate	0.7740	0.8457
K/√Ca		0.7739	0.8451
K/√Ca + Mg	Mehlich 3	0.7965	0.8149
K/√Ca		0.7952	0.8100

Table 6. Correlation between adjusted Mg-characteristics of soil tests and nutrients in barley shoots

Magnesium value transformation	Soil test (extractant)	Correlation coefficient (*r*)	
		Mg-concentration in barley	Mg-uptake
Mg/K (mg/kg)	water	0.7258	0.7248
Mg/K (mg/kg)	NH$_4$-acetate	0.7577	0.5334
% Mg-equivalents in CEC		0.5604	0.5703
Mg/K (mg/kg)	Mehlich 3	0.7884	0.5384

to avoid an error in the subsequent process of agronomic interpretation of soil tests for the needs of fertilisation (Matula and Pechová 2005).

The best coincidence between soil test and phosphorus in plant was observed in water extraction of soils at a 1:5 ratio (w/v). We confirmed again improvement of coincidence between soil and plant in NH$_4$-acetate soil test after the transformation of determined phosphorus in the soil extract to phosphorus index, the product with calculated CEC value, which is also a part of NH$_4$-acetate soil test (Matula 1996, Matula 1999). In Mehlich 3 soil test we observed a trend of better coincidence with phosphorus in plant when phosphorus was determined in the extract of colorimetric phospho-molybdate blue method in a Skalar analyser (Tables 4 and 7). It could be caused by an aggressive extractant used in Mehlich 3 that penetrates deeper into the fractions of phosphorus reserve in soil, extracts more stable fractions of organic phosphorus, not available to plants, which is determined by ICP detection but is not identified by colorimetric detection.

Manganese. Mehlich 2 soil test was declared as a universal extractant for the determination of P, K, Mg, Ca, Na, Mn and Zn (Mehlich 1978). Mehlich 3, its modification by addition of EDTA, besides a reduction in the corrosivity of the agent by substitution of HNO$_3$ for HCl, was to extend its universality by determination of the trace element copper (Mehlich 1984). These assumptions were based only on relation to other soil tests; unfortunately, the correlation with real bioavailability, which is however crucial, was neglected.

Table 7. Correlation between P-characteristics of soil tests and nutrients in barley shoots

Phosphorus characteristics	Soil test (extractant)	Correlation coefficient (*r*)	
		concentration in barley	nutrient uptake
Colorimetric determination (mg/kg)	water	0.8063	0.8470
Colorimetric determination	NH$_4$-acetate	0.4953	0.6608
P-index (ICP) (mg/kg)		0.5682	0.7554
Colorimetric determination P-index (colorimetric) (mg/kg)		0.5965	0.7758
	Mehlich 3	0.5303	0.6927

Table 8. Determined P-values in extracts of soil tests by ICP and colorimetric detection

Determination	ICP	Colorimetric
P-soil test (extractant)	mean values (mg P/kg)	
Water	3.77	2.91
NH_4-acetate	17.6	17.2
Mehlich 3	161	129

The task of soil tests should be to help rationalise the soil reserve of nutrients by fertilisation. Without a good relation of soil test to plant it is not possible to successfully develop calibration research for practical needs of plant nutrition rationalisation in the field.

We did not find any relationship between Mehlich 3 soil test and manganese in plant (Table 4). It is logical because the acid character of the extractant (pH < 2.9) radically intervenes in natural soil chemistry and creates conditions for the conversion of trivalent and quadrivalent oxides of manganese, unavailable to plants, to Mn^{2+} that are detected and do not correspond to available Mn^{2+} in the actual status of soil chemistry. We can imagine the extraction aggressiveness of Mehlich 3 extractant if we compare the given values of manganese in Tables 1–3. Soil tests of water and NH_4-acetate extraction influence the natural soil chemistry minimally, which will be reflected in the high coincidence of Mn values determined in soil with Mn in plant (Table 4).

Boron. The highest coincidence of soil test with boron in plant was found in NH_4-acetate extraction followed by water extraction. Mehlich 3 soil test was not in a good relation with boron in plant; so we cannot assume its functionality in preventive diagnostics of boron in the field. The cause of the bad relation of boron in Mehlich 3 extract to boron in plant can be seen in the radical intervention of the extractant in natural soil chemistry. In general, it is known about boron that its uptake from soil depends on the pH value of soil (Russell 1973, Tisdale and Nelson 1975, Mengel and Kirkby 1982, Gupta et al. 1985, Goldberg 1997). A part of the soil test with NH_4-acetate extraction is to define a suitable range of soil pH and its percentage deviations from the actually determined pH value. The need of liming is based on deviations of actual pH from the desirable pH value (Matula and Pechová 2006). The lower value of suitable soil pH is calculated in relation to the CEC value of soil ($2.9 \times CEC^{0.14}$). The correction of the determined value of boron by the coefficient expressing the deviation of actual pH from the desirable pH value (Matula and Pechová 2006) improved the closeness of the relation of NH_4-acetate soil test to boron in plant (Table 4).

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Received on February 16, 2009

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