Boron sorption in soils and its extractability by soil tests (Mehlich 3, ammonium acetate and water extraction)

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ABSTRACT

The aim of the paper was to contribute to the acquisition of background data for the specification of safe boron levels in soils in relation to diagnostics by multi-nutrient soil tests and to CEC (cation exchange capacity) value of soil, pH and soil organic matter. The research was conducted on 24 soils. Sorption was determined after 97 days from the application of B at the rates of 0, 1, 2.5, 5 mg B/kg in H_3BO_3. The closest regression of B-sorption was with the CEC value of soil in NH_4-acetate and water tests and it increased with the increasing application of B (regression at a rate of 5 ppm B; NH_4-acetate: linear $R^2 = 0.632$, polynomial 2nd $R^2 = 0.644$; water: linear $R^2 = 0.644$, polynomial 2nd $R^2 = 0.599$). No relationship was found in the Mehlich 3 test. Regressions of B sorption on pH value were substantially lower. The relationship of B sorption with soil organic matter was similar to CEC, but less close. In the NH_4-acetate soil test, after the correction of CEC value of soil by pH deviations from the optimum, regression was improved (linear $R^2 = 0.821$, polynomial 2nd $R^2 = 0.837$).

Keywords: boron in soil; sorption; soil tests; Mehlich 3; ammonium acetate extraction; water extraction; CEC value; pH value; soil organic matter; quantification of relations

A specific feature of boron in plant nutrition, compared to other nutrients, is an extremely narrow range between deficit and surplus, the latter being expressed by toxicity. This aspect should always be taken into account when boron nutrition of plants is adjusted by fertilization.

The majority of the soils in the Czech Republic are naturally deficient in boron. Boron is easily leached from the soil. Boron-deficient soils are mainly podzolized, light, (acid) soils in humid areas or overlimed soils with a high content of carbonates ($CaCO_3$).

Plants react directly to the activity of boron in a soil solution and indirectly to boron adsorbed to soil components, i.e. aluminium and iron hydroxides, clay minerals, calcium carbonates and organic components. The following soil parameters influence boron availability to plants from the soil: pH value, structure, moisture, temperature, organic matter and clay mineralogy (Russell 1973, Gupta et al. 1985, Keren 1996, Goldberg 1997). The role of organic matter in boron adsorption and desorption processes in the soil has not been fully understood yet. Organic matter is assumed to reduce the intensity of boron adsorption by coating the surfaces of mineral components of soil, thereby limiting direct contact with adsorption sites (Marzadori et al. 1991). Boron sorption in soils is influenced most markedly by the pH value. With the increase in pH value, adsorption also increases and reaches a maximum under alkaline conditions (Russell 1973, Keren 1996). Soils low in clay adsorb less boron than clay-rich soils. Adsorption capacity differs between clay minerals; illites are the most reactive and kaolinite is the least reactive. Boron is mainly adsorbed at marginal positions of the layers of clay minerals (Keren 1996). Cation exchange capacity of soil (CEC value) is an important characteristic to assess the boron status of soil (Raza et al. 2002). The degree of cation saturation also influences boron adsorption. Especially soils with high potassium saturation fix boron more strongly (Gupta et al. 1985). The liming of acid soils enhances boron adsorption. Active forms of aluminium [Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$] are displaced from the

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sorption complex by calcium (Ca^{2+}). Precipitates of deactivated aluminium [$Al(OH)_3$], outside the sorption complex of clay minerals, are strong adsorbents of boron onto their surfaces.

Preventive indication of the boron status in soil by soil tests is important for the rationalisation of field fertilization. Conventionally, since 1939 hot water extraction in different modifications was used for boron assessment in the soil (Johnson and Fixen 1990, SPAC 1999); this soil test however presents a number of methodical difficulties adversely influencing the standard character of results. A possibility of including boron in multi-nutrient soil tests (Mehlich 3, extraction with water and ammonium acetate) was tested by Matula and Pechová (2006). The closest correlation between soil and plant was determined in ammonium acetate extraction and in water extraction. The Mehlich 3 soil test did not prove a possibility of use for boron diagnostics in soil.

The aim of experiments presented here was: to contribute to the specification of safe (nontoxic) levels of boron reserve in different soils; to find out differences in boron sorption in soils after the application of differentiated boron rates in relation to the detection of extractable boron by multi-nutrient soil tests; to quantify more exactly the relationship of boron sorption in different soils and to examine possibilities of generalizing such quantification in relation to significant parameters of soils (i.e. CEC value, pH and organic components) that are considered as dominant factors of boron sorption in soils and its availability to plants but as yet lacking necessary quantification.

MATERIAL AND METHODS

Soil samples of the topsoil of farmed fields were used for the study. Soil samples were sieved through a 2 mm screen and dried at a natural air temperature. A set of 24 soils of the topsoil of farmed fields was selected from a collection of soils so that it would cover the largest possible range of the values of cation exchange capacity (CEC), pH value and so that it would also comprise marked differences in the initial content of labile boron in soils. The range of values in the selected set of soils was 47–312 mmol+/kg for CEC values and 3.94–6.54 for pH (0.2M KCl). As the soils of farmed fields usually have a low boron reserve, it was not possible to acquire a set with a wider range of soil boron content. Table 1 shows the agrochemical characteristics of the 24 soils selected.

An incubation experiment with a daily variable cycle of temperatures (10°C for 8 h, 15°C for 16 h) was conducted with the 24 soils. Four treatments of boron addition, each replicated threefold, were established for each soil: 0 – control; 1 ppm B; 2.5 ppm B; 5 ppm B. Soil incubation was carried out in plastic pots of 6 cm in diameter and 6 cm in height, each pot being filled with 50 g soil. The respective rates of boron were applied in 10 ml of H_3BO_3 solution. Slight deviations from the planned additions were revealed by the analytical control of B concentrations in application solutions (0.957 ppm B; 2.406 ppm B; 4.976 ppm B). The pots were loosely covered with lids on the first three days to allow the soil to dry out. After this had occurred, the soil was thoroughly mixed using a spatula and the soil moisture adjusted with distilled water by weighing until field water capacity was reached when the pots were sealed up. Incubation period lasted for 97 days during which the field water capacity was checked and adjusted from time to time.

Three soil tests were used to evaluate the nutrient status of soils: Mehlich 3 (Zbíral 2002), water extraction 1:5 w/v (SPAC 1999) and extraction with 0.5M ammonium acetate with addition of ammonium fluoride (Matula 1996). The content of oxidizable organic matter was determined according to Sims and Haby (1971). The ICP-OES technique (Thermo Jarrell Ash Trace Scan Analyzer) was used for the detection of boron and other nutrients.

Experimental results were evaluated by statistical programmes GraphPad PRISM, Ca., USA, version 2 and Microsoft Excel 2003.

RESULTS AND DISCUSSION

Figures 1–3 illustrate the results of extraction of the entire set of 24 soils by soil tests after 97 days of incubation from the application of the different boron rates. The values of boron extraction from the soil increased practically linearly with the increasing rate of boron in all soil tests but very individually in the particular soils. The values of boron from extractions with NH_4-acetate and with water were very similar whereas the values determined by the Mehlich 3 soil test were substantially higher. The extraction strength of Mehlich 3 test in the control (i.e. without B application) was five times higher as compared to NH_4-acetate and water extractions. Sorption of B from the applied B rate differed depending on

Table 1. Information about agrochemical characteristics of the experimental set of soils

Soil	Locality of soils	pH (0.2M KCl)	CEC (mmol+/kg)	C_{ox} (%)	Soil tests (mg B/kg)			
					Mehlich 3	NH_4-acetate	water (1:5)	hot water
1	Slatiny	4.98	309	2.35	1.391	0.360	0.946	2.234
2	Slatiny	6.50	275	2.24	2.473	0.642	0.328	2.459
3	Liběšice	5.77	267	1.74	1.569	0.364	0.356	1.735
4	Liběšice	5.19	208	1.17	1.107	0.296	0.548	1.163
5	Koloveč	5.39	153	1.68	0.783	0.186	0.135	0.600
6	Bečváry	6.37	145	1.04	1.009	0.238	0.149	0.701
7	Výčapy	5.65	143	1.34	0.926	0.218	0.300	0.859
8	Č. Janovice	5.17	138	1.07	0.762	0.158	0.246	0.584
9	Opava	6.54	121	1.09	1.254	0.402	0.203	0.886
10	Bečváry	6.42	104	1.16	1.183	0.302	0.209	0.763
11	Třebohostice	4.65	89	1.07	0.680	0.152	0.132	0.344
12	Sychrov	4.99	48	0.79	0.685	0.126	0.097	0.202
13	Slatiny	5.48	294	2.29	1.875	0.384	0.284	1.409
14	Nový Jičín	5.40	265	1.96	1.943	0.342	0.530	1.432
15	Slatiny	4.54	214	1.62	2.015	0.234	0.305	1.314
16	Liběšice	4.33	170	1.09	1.612	0.228	0.306	0.830
17	Bečváry	6.37	141	1.01	1.814	0.362	0.196	0.711
18	Č. Janovice	6.16	138	0.96	1.527	0.340	0.245	0.873
19	Č. Janovice	5.40	131	1.92	2.233	0.252	0.184	0.602
20	Výčapy	5.15	132	1.03	1.316	0.238	0.304	0.625
21	Liběšice	6.23	117	0.99	1.701	0.468	0.290	0.814
22	Třebohostice	5.40	104	1.16	1.198	0.230	0.107	0.243
23	Chyše	3.94	94	1.01	1.162	0.202	0.189	0.401
24	Sychrov	4.80	49	0.52	1.458	0.188	0.093	0.137

CEC – cation exchange capacity; C_{ox} – oxidizable carbon

the soil test used. It amounted to 61% on average in the NH_4-acetate and water extractions while it was 55% in the Mehlich 3 extraction. The sorption values in all three soil tests slightly decreased with the higher rate of applied B.

The regression of B sorption in relation to B rate in particular soils and in the framework of their detection by soil tests was very close (R^2 for regression of the 2nd degree polynomial ranged from 0.997 to 1; R^2 for linear regression was 0.993). The value of these calculated close regression relations is however low in relation to the needs of a soil test. The main reason of this is the practical application of soil test for preventive prognosis of the nutrient status which assumes universality for a broad spectrum of different soils without the necessity of developing varied agronomic interpretation relating to specific features of the particular soils.

Dominant factors influencing boron sorption in soil, as well as its availability to plants, are as

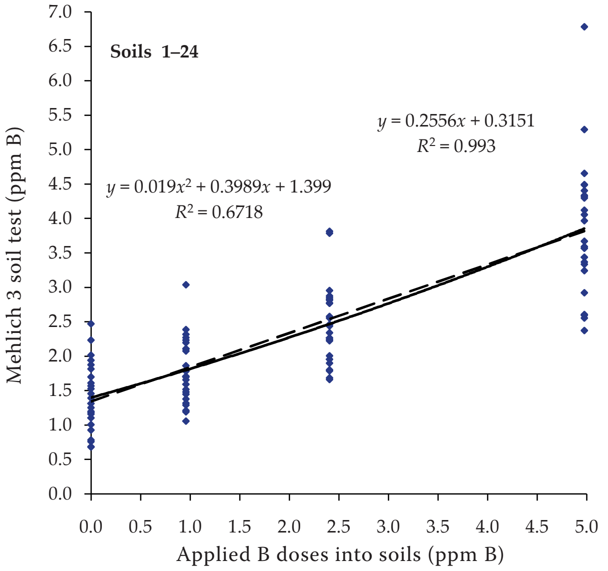

Figure 1. The relationship between doses of boron applied into soils and boron determined in soils by the Mehlich 3 soil test after 97 days from B application into soils

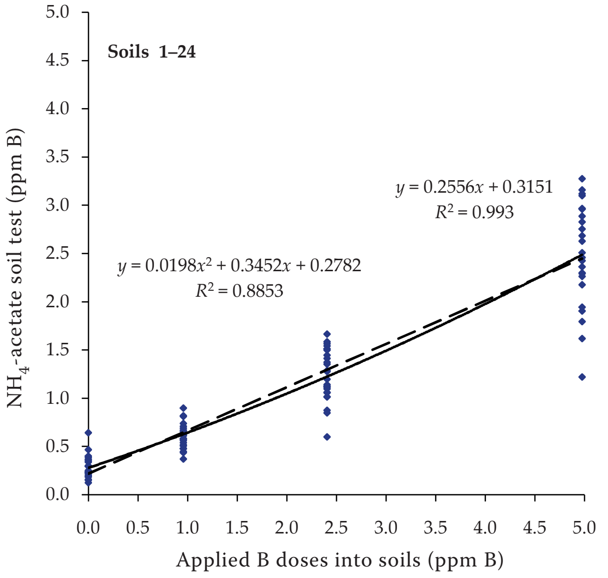

Figure 2. The relationship between doses of boron applied into soils and boron determined in soils by the NH_4-acetate soil test after 97 days from B application into soils

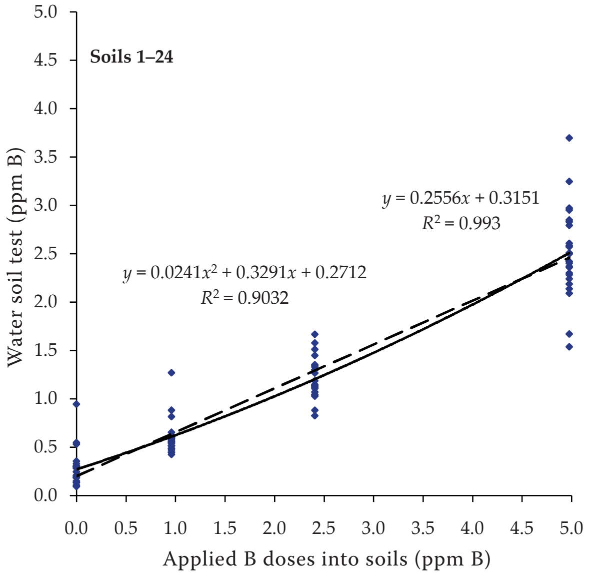

Figure 3. The relationship between doses of boron applied into soils and boron determined in soils by the water (1:5) soil test after 97 days from B application into soils

follows: soil mineralogy – clay minerals, pH value of the soil and content of soil organic matter. Raza et al. (2002) considered the CEC value of soil as an important characteristic to evaluate the boron status in soil. An advantage of the CEC value is that it indicates both the quantity and the quality of sorbent soil minerals. This is applicable mainly to the conditions of the CR soils, where the content of soil organic matter is low, and so its participation in the cation exchange capacity is not significant. The relations of the nutritive status of boron in soil to the above-mentioned factors are given more or less in general terms, without necessary quantification of the relationships.

Therefore, the relationships between the three multi-nutrient soil tests and important characteristics of soils (CEC, pH and oxidizable organic matter) will be demonstrated in the results presented below. Generalizing relations may be expected provided that they could contribute to

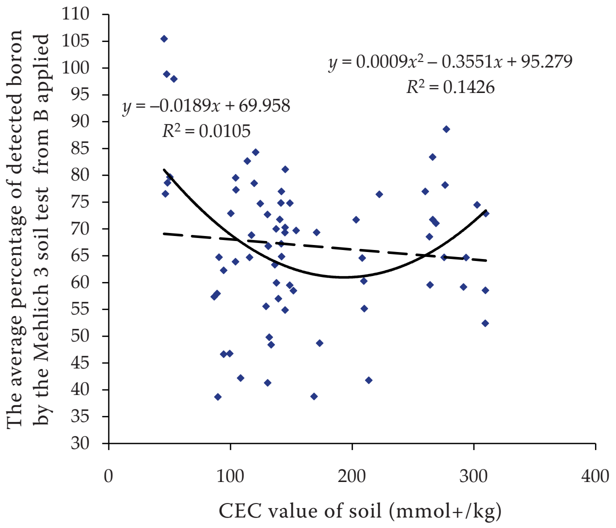

Figure 4. The dependence of the ratio of detected B to B applied into soil by the Mehlich 3 soil test on the CEC value of soil

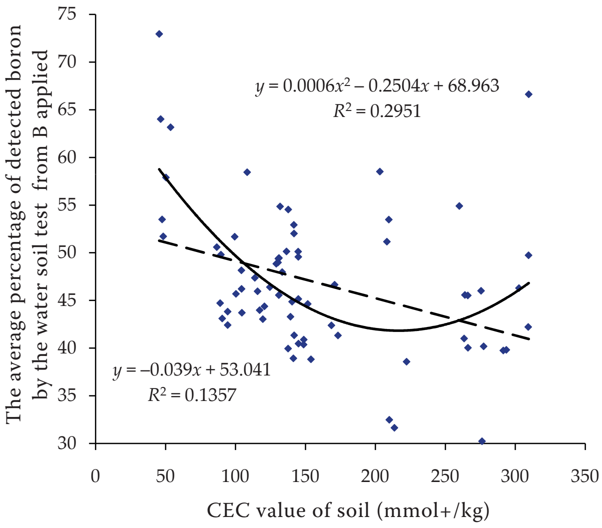

Figure 5. The dependence of the ratio of detected B to B applied into soil by the water soil test on the CEC value of soil

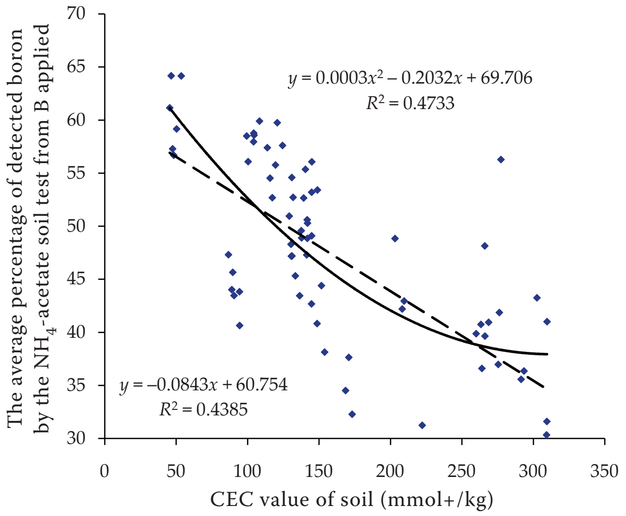

Figure 6. The dependence of the ratio of detected B to B applied into soil by the NH$_4$-acetate soil test on the CEC value of soil

the more universal use of multi-nutrient soil tests for the specification of boron reserve in the soil for plants.

Relationship to CEC of soil. Figures 4–6 document the trends of a relationship between CEC value of soils and percentage of detected boron from applied boron by soil tests (without considering the specification of boron rate). The closest trend of the relationship with CEC value of soil was determined by the soil test using NH$_4$-acetate extraction. The Mehlich 3 soil test was of no practical value. A substantially better trend of regression was found in water extraction of soil (1:5).

The trends of the closeness of relations were markedly different when the specific boron rate was taken into account in the extractions with NH$_4$-acetate and water. The closeness of the relationship increased with the increasing rate of boron applied to soils (Table 2). Our results support the idea of the dominant role of clay minerals in sorption, facilitating boron availability to plants.

Relationship to pH of soil. Opposite trends of the relationship and much less close than for the CEC value of soil were determined in regressions between extracted boron from the soil by soil tests and soil pH value. By contrast to the CEC relationship the closeness was the highest in the application of the lowest boron rate (1 ppm). See Figures 7–9 and Table 3.

Relationship to soil organic matter. The observed trends of the relationship between extracted boron from the soil by soil tests and the value of oxidizable carbon (C$_{ox}$) were similar to those of the relationship with CEC value of soil. Table 4 shows these relationships. Similarity of the relations is logical because in soils of the CR with

Table 2. Regression between B determined by soil tests after the application of different B rates and CEC value of soils

Rate H$_3$BO$_3$ (ppm B)	NH$_4$-acetate extraction		Mehlich 3 extraction		Water (1:5) extraction	
	linear R^2	polynomial 2nd degree R^2	linear R^2	polynomial 2nd degree R^2	linear R^2	polynomial 2nd degree R^2
1–5	0.4385	0.4733	0.0105	0.1426	0.1357	0.2951
1	0.2068	0.2630	0.0030	0.1370	0.0321	0.1768
2.4	0.5152	0.5617	0.0137	0.1762	0.2409	0.4564
5	0.6316	0.6439	0.0506	0.2420	0.4734	0.5987

Table 3. Regression between B determined by soil tests after the application of different B rates and pH (0.2M KCl) value of soils

Rate H$_3$BO$_3$ (ppm B)	NH$_4$-acetate extraction		Mehlich 3 extraction		Water (1:5) extraction	
	linear R^2	polynomial 2nd degree R^2	linear R^2	polynomial 2nd degree R^2	linear R^2	polynomial 2nd degree R^2
1–5	0.2047	0.2055	0.1429	0.1432	0.0757	0.2246
1	0.3812	0.3955	0.1708	0.1728	0.0562	0.2938
2.4	0.1882	0.1885	0.2141	0.2141	0.0931	0.2689
5	0.1279	0.1279	0.1802	0.1854	0.0871	0.1836

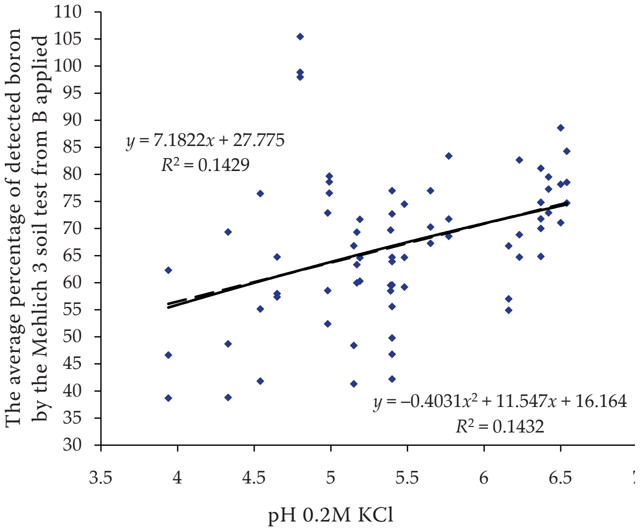

Figure 7. The dependence of the ratio of detected B to B applied into soil by the Mehlich 3 soil test on the pH value of soil

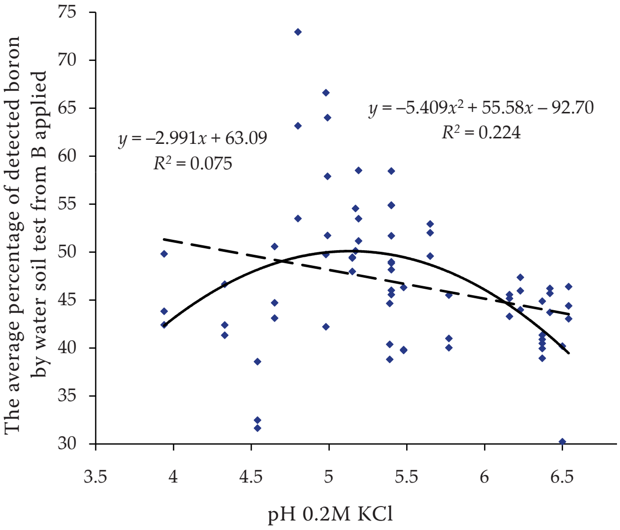

Figure 8. The dependence of the ratio of detected B to B applied into soil by the water soil test on the pH value of soil

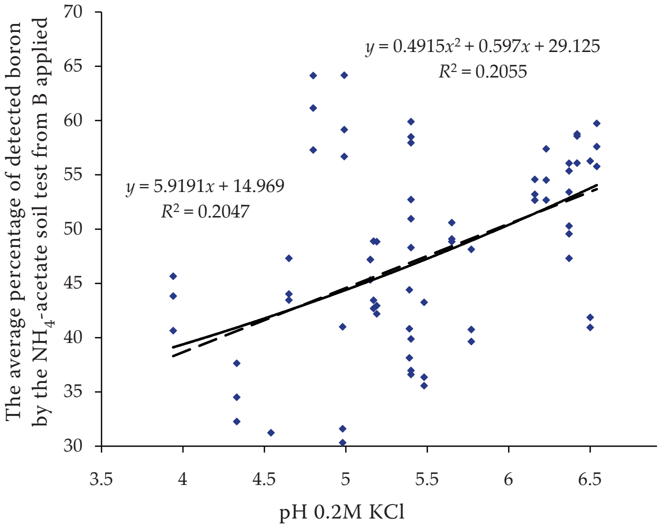

Figure 9. The dependence of the ratio of detected B to B applied into soil by the NH_4-acetate soil test on the pH value of soil

the long history of farming clay minerals have a protective position of the organic component bound to clays before its further mineralization. The closeness of the relationship between CEC value of soil (which is in fact influenced by the proportion of clay minerals in soil in conditions of the CR) and C_{ox} of the experimental set of soils is demonstrated in Figure 10.

Possibilities of defining a change in the boron value of soil test as recalculated after the application of 1 ppm B to soil. Previous results indicate a dominant position of the CEC value of soil in boron sorption in soil, which is in agreement with Raza et al. (2002), with a substantially smaller influence of the soil pH value. Quite satisfactory regression relations were found in the soil test by extraction with ammonium acetate and water (Figures 11 and 12). The Mehlich 3 test showed a fully unsatisfactory trend of the relationship (Figure 13).

Table 4. Regression between B determined by soil tests after the application of different B rates and soil organic matter

Rate H_3BO_3 (ppm B)	NH_4-acetate extraction		Mehlich 3 extraction		Water (1:5) extraction	
	linear R^2	polynomial 2nd degree R^2	linear R^2	polynomial 2nd degree R^2	linear R^2	polynomial 2nd degree R^2
1–5	0.3363	0.3654	0.0220	0.1430	0.1297	0.2038
1	0.1905	0.2358	0.0005	0.1267	0.0155	0.1529
2.4	0.3324	0.4123	0.0181	0.2451	0.2359	0.3882
5	0.4821	0.4919	0.0572	0.2307	0.3617	0.4410

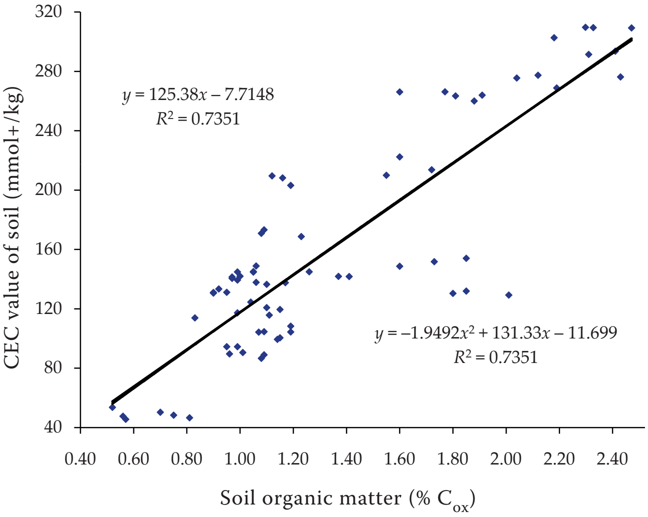

Figure 10. The relationship between soil organic matter and the CEC value of soil

The definition of adequate pH of soil in relation to the CEC value of soil for the needs of soil liming specification in the field (Matula and Pechová 2002) is a part of the soil test by ammonium acetate extraction. In Matula and Pechová (2006) in the NH_4-acetate soil test, a correction of the determined value of boron by the ratio of deviations of actual pH from required pH substantially improved the relationship between boron in soil and its content in plants. These previous results inspired us to add the participation of pH into the relationship between CEC value of soil and reaction of NH_4-acetate soil test to B application to soil. The closest relation between CEC value and reaction of soil test to B application was reached after the correction of CEC value by subtracting the pH deviation from the required optimum. The

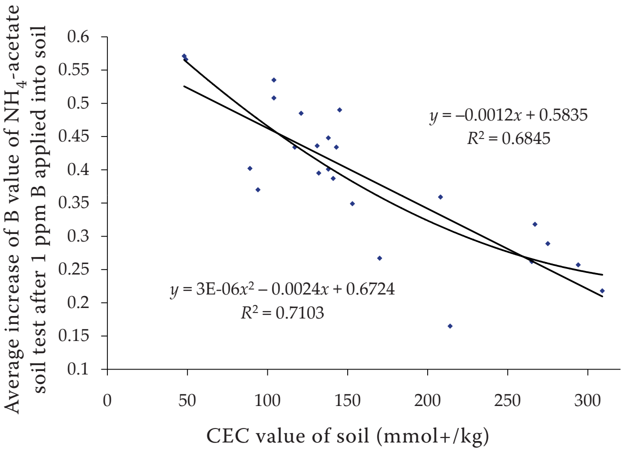

Figure 11. The reaction of the NH_4-acetate soil test to the unit of boron applied into soil in dependence on the CEC value of soil

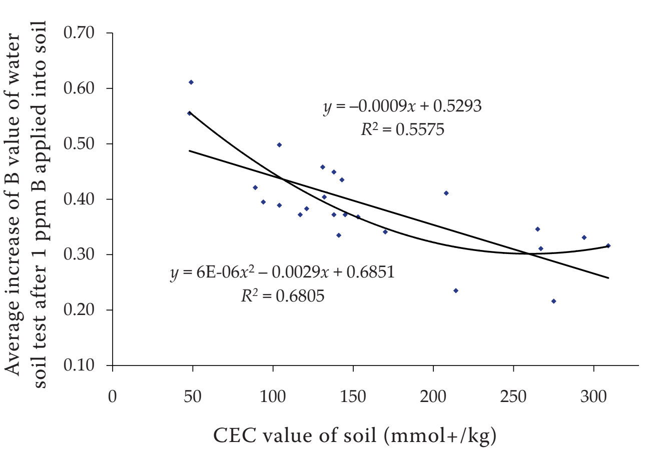

Figure 12. The reaction of the water soil test to the unit of boron applied into soil in dependence on the CEC value of soil

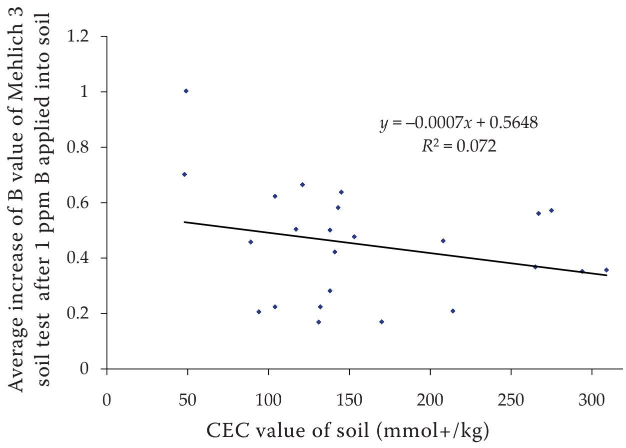

Figure 13. The reaction of the Mehlich 3 soil test to the unit of boron applied into soil in dependence on the CEC value of soil

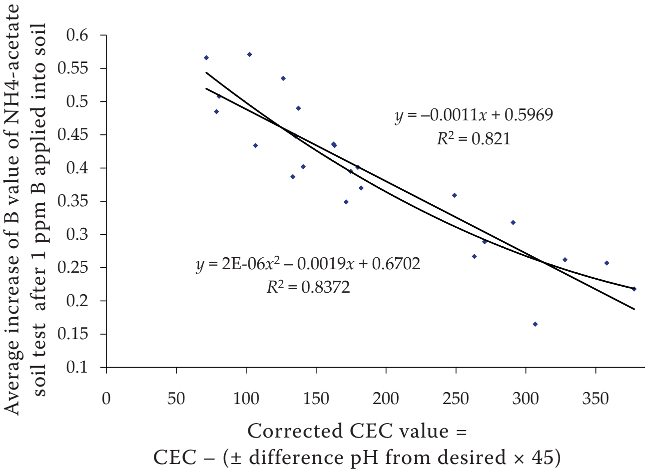

Figure 14. The reaction of the NH_4-acetate soil test to the unit of boron applied into soil in dependence on the corrected CEC value of soil by pH difference from desired pH value

following method of calculating the correction of the CEC value of soil was used: $CEC_{corrected}$ = CEC – (±pH difference from lower optimum × 45), see Figure 14. The lower value of adequate pH of soil was defined by the relation: $pH = 2.9 \times CEC^{0.14}$ (Matula and Pechová 2002). Such closeness of the relation is applicable to specify the need of boron fertilization for an adjustment of the required B status in different soils by means of NH_4-acetate soil test diagnostics.

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