ROCZNIKI GLEBOZNAWCZE T. XIII, Z. 2, WARSZAWA 1963

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AVAILABILITY OF BORON IN SOILS AND THAT ABSORBED ON ANION EXCHANGE RESIN AND LIGNIN[2]

In soils one may distinguish total, acid-soluble and water-soluble boron. The total amount of boron in soils is of a minor interest from the agricultural point of view because only a small part of it is readily available to plants. The extraction of available boron with boiling water described by Berger and Truog [1] is commonly used by investigators in this field. Philipson [8] came to the conclusion that the boiling water extraction gives an idea of the quantity at the immediate disposal of plants but does not give an adequate idea of the reserves of boron in the soil which may become soluble and available. He developed a method of extraction of available boron in soils using a phosphoric acid solution of pH 2.8 or lower, and clamis this method gives a truer expression of the boron situation in the long-term perspective.

In the experiments herewith described, the availability of boron remaining in two soils after extraction with boiling water and dilute phosphoric acid and also the boron absorbed on anion exchange resin and lignin was investigated.

MATERIALS AND METHODS

Sunflowers (*Helianthus annus L.*, var. *Mammoth Russian*) were grown in the greenhouse in four liter plastic pots each of which contained 5 kg of quartz sand, and other additions later described. At the beginning of the experiment onehalf liter of modified Hoagland's nutrient solution [3] without boron was added to each pot. During the growing period most of the pots (those with the larger plants) received an additional one liter of similar nutrient solution. Only onehalf liter of Hoagland's modified nut-

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rient solution was added to the two treatments showing early boron deficiency and having small plants. This reduction to 0.5 liter was done to prevent a too high concentration of salts in solution. Reagent grade chemicals and demineralized water containing only 0.02 mg B/l was used. The restricted or negligible growth of the plants in the pots to which boron was not purposely added is proof that the content of boron as impurities in the water and chemicals used did not appreciably affect the plants.

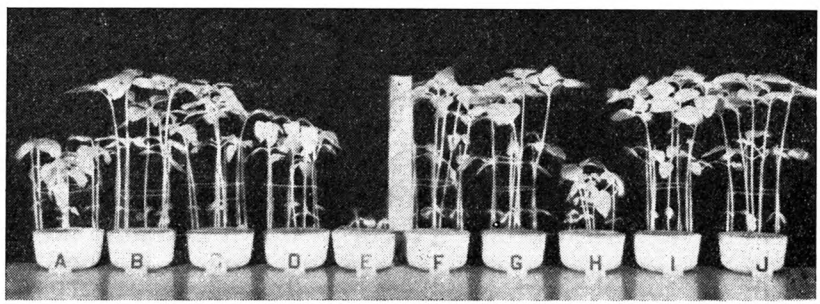

Figure 1. Sunflower grown in quartz sand with addition of boron from different sources. *A* — control, *B* — borax, *C* — subsoil, *D* — water extracted subsoil, *E* — H_3PO_4 extracted subsoil and then limed, *F* — muck soil, *G* — water extracted muck soil, *H* — H_3PO_4 extracted muck soil and then limed, *I* — boron absorbed on anion exchange resin, and *J* — boron absorbed on lignin

Słonecznik uprawiany w piasku kwarcowym do którego dodano bor w różnych postaciach: *A* kontrolne — bez boru, *B* — boraks, *C* — podglebie, *D* — podglebie wyekstrahowane wodą, *E* — podglebie wyekstrahowane H_3PO_4 i potem zwapnowane, *F* — gleba murszowa, *G* — gleba murszowa wyekstrahowana wodą, *H* — gleba murszowa wyekstrahowana H_3PO_4 i potem zwapnowana, *I* — bor zaadsorbowany na żywicy wymiennej, *J* — bor zaadsorbowany na ligninie

The characteristics of the two soils added to the quartz sand are given in table 1. The soils had been pulverized so as to pass a 20-mesh sieve. The available boron was determined by the boiling water extraction. The Seaton silt loam subsoil had been taken at a depth of 15—20 feet, and the Carlisle muck was surface material. The pH values given in table 1 were determined in a soil-water paste with a glass electrode. Available nitrogen was determined by alkaline permanganate digestion [9]. Available phosphorus and potassium were determined by extraction with 0.3 N-HCl [6].

In experiment I, additions to the quartz sand of borax and the two soils (extracted and not extracted) and of boron absorbed on anion exchange resin (Dowex 2x) and on lignin are given in detail in table 2. All treatments were made in quadruplicate. The amount of available boron in the soils was determined by the boiling water extraction method. Extraction of the soils (added to the pots) with boiling distilled water (ratio soil

Table 1

Charecteristics before and after extraction of the two soils added to the quartz sand

Soil	pH	Available			
		B	N	P	K
		mg/kg	ppm		
Seaton silt loam subsoil	7.9	0.742	12.5	11.5	42.5
Seaton silt loam subsoil extracted with boiling water	8.2	-	12.5	9.5	37.5
Seaton silt loam subsoil extracted with H_3PO_4	6.5	-	12.5	175.0	55.0
Carlisle muck	6.7	4.930	1400	360.0	360.0
Carlisle muck extracted with boiling water	6.9	-	1400	380.0	200.0
Carlisle muck extracted with H_3PO_4	3.6	-	1400	1160.0	100.0

Table 2

Yields, boron content and total amount of boron uptake by sunflower plants

Treatment of quartz culture	Dry matter g/pot	Boron in µg per g of dry matter	Total amount of B uptake in µg per pot
Control (quartz sand) no $Na_2B_4O_7$	8.0	16.0	128.0
0.2 mg B/pot as $Na_2B_4O_7 \cdot 10H_2O$	12.6	20.9	263.3
270 g of Seaton silt loam subsoil per pot giving 0.2 mg available boron	11.0	18.5	203.5
270 g of Seaton silt loam subsoil extrated with boiling water per pot	8.5	17.5	148.8
270 g of Seaton silt loam subsoil extracted with H_3PO_4 per pot	1.9	17.1	32.5
40.6 g muck soil per pot giving 0.2 mg available boron per pot	15.3	33.4	511.0
40.6 g muck soil extracted with boiling water per pot	14.9	27.7	412.7
40.6 g muck soil extracted with H_3PO_4 per pot	5.7	16.5	94.1
0.2 mg absorbed on 0.533 g anion exchange resin per pot	15.0	25.7	385.5
0.2 mg B absorbed on 4.082 g lignin per pot	14.5	26.3	381.4
L.S.D. (0.05)	1.2	-	-

to water 1 : 2) was for 5 minutes with a refluxing condensor; they were then washed several times on a Büchner funnel and dried at room temperature. Other portions of each soil were extracted with dilute phosphoric acid ($\frac{1}{20}$ and $\frac{1}{50}$ malar depending on original acid neutralizing capacity of the soil) so as to give a pH of 2.8 to the final extracting solution. In case of the Seaton subsoil it was $\frac{1}{20}$ M H_3PO_4 and in the case of the Carlisle muck soil it was $\frac{1}{50}$ M H_3PO_4. After extraction the soils were washed on a Büch-

ner funel about 10 times with distilled water and then dried at room temperature. The Carlisle muck extracted with phosphoric acid remained strongly acid even after prolonged washing as shown in table 1. Samples of these soils were titrated with $Ca(OH)_2$ and an equivalent amount of $CaCO_3$ was added to them so as to adjust their pH to that of the non-extracted soils.

The anion exchange resin (Dowex 2x [3] obtained from Dow Chemical Co- Midland, Michigan) was dried, ground and passed throught a 100 mesh sieve. After wetting with water, 6 ml of wet resin was transferred to a glass column 1 cm in diameter. Through this column was passed slowly 10 ml of borax solution containing 1 g B/l. The resin was then washed several times with distilled water and dried at room temperature. The amount of boron adsorbed by the resin was determined as follows: a 400 mg sample of the resin was transferred to a small column, and 30 ml of 2 N HCl was passed through. The filtrate was collected in a 1000 ml volumetric flask and the amount of boron present in the filtrate was determined. An additional 15 ml of 2 N HCl was passed through the column and the filtrate was collected in a 250 ml volumetric flask. This filtrate was found to be free of boron, showing that the previous extraction was complete.

Alkali lignin (Indulin A) [4] produced by West Virginia Pulp and Paper Company was used. Fifty grams of this lignin was treated in a beaker with 500 ml of borax solution containing 1 g B/l and let stand overnight. The amount of boron present was then determined after ignition using the curcumin procedure [2]. Each treatment (five plants per pot) was quadruplicated. Careful, daily observations were made during the growing period. The plants were harvested after one month of growth. The roots were washed first in tap then in distilled water and all the material dried at 80 °C. Finally the plants were weighed, then ground in a Wiley mill and after ignition the boron was determined by the curcumin procedure [2].

RESULTS AND DISCUSSION

Table 2 gives the results of experiment I. The data show that boiling water extraction of soils very low in organic matter removes almost all boron available for plants. This is not true in the case of soil high in organic matter. There was no significant difference in yield of plants grown with

[3] Strongly basic anion exchanger.

[4] Indulin A is naturally occurring polymer, characterized by a series of closely linked benzene, pyrane and furane rings carrying methoxyl, hydroxyl and other substituent groups.

addition of not-extracted and boiling water-extracted muck soil. The amount of boron uptake by plants from treatments which received boiling water-extracted muck soil was much higher than in the control. Some boron is probably quite tightly bound in organic matter and not easily extractable by boiling water. It may become available to plants after decay of the organic matter during the growing period.

Yields in treatments with boron absorbed on anion exchange resin and on lignin were even higher than in the treatment with borax. Plants were able to obtain more boron when it was added in the form absorbed on anion exchange resin or lignin than as a form of borax. In quartz sand, there may be present some active silica which may react with calcium from the nutrient solution and form secondary minerals. In this case fixation of boron is possible as was shown by Parks and Shaw [7]. Small utilization of boron in sand culture was shown also by Majewski and Majewska [4]. When the boron was added in anion exchange form on resin and lignin, its fixation was probably less than when added as borax.

The lowest yields of plants were obtained in treatments with subsoil and muck soil previously extracted with phosphoric acid. The amount of boron uptake by plants was much lower than in the control. Very pronounced boron difficiency symptoms occurred in very early stages of growth (figure).

In these treatments, after the acidification of the soils to pH 2.8, probably a higher amount of aluminum and silica became active. After addition of $CaCO_3$ to adjust the pH to the value as in nonextracted soil, the boron could have been fixed due to the formation of secondary minerals in which substition of boron for aluminum was possible. This mechanism of fixation was suggested by Parks and Shaw [7]. Also Midgley and Dunklee [5] investigating the effect of liming on the fixation of borates in soils found that a change of pH from 5 to 6 caused a high increase in boron fixation. In this pH range aluminum become less active and may be precipitatet, forming with silica and calcium the secondary minerals in which substitution of boron for aluminum is possible. In the soils extracted with phosphoric acid, the amount of available phosphorus (table 1) was much higher than in non-extracted soils. There was the possibility that this higher amount of phosphorus might influence the uptake of boron. To investigate this possibility, an experiment II with a different amounts of phosphorus in the nutrient solution was carried out in cultures similar to those in the previous experiment. Results of experiment II are given in table 3.

From the data in table 3 make it apparent that two and eight times the normal phosphorus concentration in modified Hoagland's solution

did not significantly affect the yields of sunflower. These results indicate that the marked decrease of yield in treatments with soils extracted with phosphoric acid was not due to a higher amount of phosphorus in these treatments.

Table 3

Influence of high level of phosphorus on availability of boron and growth of sunflower

Treatments of quartz cultures	Dry matter g/pot
Control	9.7
Borax	13.9
Borax + 2 times the normal phosphorus concentration	14.3
Borax + 8 times the normal phosphorus concentration	12.7
L.S.D. (0.05)	1.7

On the basis of these data it is impossible to compare the boiling water extraction method with Philipson's method. It seems that in the case of soils low in organic matter, the extraction by boiling water may remove most of the boron readily available to plants. Generalization of this reqires tests with more soils. Boiling water extraction of soils high in organic matter does not give the exact information of the available boron situation in the long-term perspective. Boron absorbed on anion exchange resin or on lignin is easily available for plants.

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DOSTĘPNOŚĆ BORU ZAWARTEGO W GLEBACH I BORU ZAADSORBOWANEGO NA ŻYWICY WYMIENNEJ I LIGNINIE

Streszczenie

Przeprowadzono doświadczenia wazonowe za słonecznikiem w celu zbadania dostępności boru zawartego w glebach oraz boru zaadsorbowanego na żywicy wymiennej i ligninie. Doświadczenie składało się z 9 kombinacji.

Wazony napełniono piaskiem kwarcowym i dodano zmodyfikowaną pożywkę Hoaglanda pozbawioną boru. Bor dodano w ilości 0,2 mg na wazon w postaci:

— boraksu,

— boru zasorbowanego na żywicy wymiennej (Dowex 2x),

— boru zasorbowanego na ligninie,

— boru zawartego w glebie mineralnej (w ilości 0,2 mg B oznaczonego metodą ekstrakcji wodą na gorąco),

— boru zawartego w glebie organicznej (również oznaczonego metodą ekstrakcji wodą na gorąco).

W pozostałych kombinacjach wprowadzono do piasku kwarcowego te same ilości gleb jak w kombinacji 4 i 5 po uprzednim wyekstrahowaniu ich wodą na gorąco lub H_3PO_4 na zimno (płyn po ekstrakcji o pH 2,8) w celu usunięcia dostępnego boru.

Na podstawie oznaczeń boru pobranego przez słonecznik stwierdzono, że w przypadku gleby mineralnej ekstrakcja wodą na gorąco (gotowanie przez 5 minut pod chłodnicą zwrotną i przemycie na zimno) usuwa prawie cały dostępny dla roślin bor. Ekstrakcja wodą na gorąco gleby o dużej zawartości substancji organicznej nie określa dokładnie ilości boru dostępnego dla roślin. Z gleby organicznej nawet po wyekstrahowaniu wodą na gorąco rośliny pobrały duże ilości boru.

W kombinacjach gdzie do piasku kwarcowego dodano glebę uprzednio ekstrahowaną rozcieńczonym H_3PO_4 i następnie zwapnowano (w celu doprowadzenia do wyjściowego pH) symptomy braku boru pojawiły się wcześniej niż w roślinach kontrolnych, rosnących na samym piasku kwarcowym. Nie było to jednak spowodowane zwiększoną ilością fosforu w tych kombinacjach, jak to wykazało dodatkowe doświadczenie ze zwiększonymi dawkami fosforu w pożywce.

Bor zasorbowany na żywicy wymiennej i ligninie był dobrze wykorzystany przez rośliny.

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ДОСТУПНОСТЬ БОРА СОДЕРЖАЩЕГОСЯ В ПОЧВАХ И БОРА АДСОРБИРОВАННОГО НА ИОНООБМЕННИКЕ И НА ЛИГНИНЕ

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Резюме

Проведена был опыт с подсолнечником для исследования доступности для растеий бора почв и бора адсорбированного на ионообменнике и лигнине. Опыт состоял из 9 вариантов.

Сосуды наполняли кварцевым песком и давали видоизменную смесь Гогланда лишенную бора. Бор давали в количестве 0,2 мг В на сосуд в форме: 1) буры, 2) бора адсорбированного на ионообменнике (Довекс 2Х), 3) бора адсорбированного на лигнине, 4) бора содержащегося в минеральной почве (в количестве 0,2 мг В, определенного по методу горячей экстракции водой), 5) бора содержащегося в органической почве (также обозначенного по методу горячей экстракции водой). В дальнйших вариантах вносили в кварцевый песок те же количества почв как в вариантах 4 и 5 но после предыдущего экстрагирования почв горячей водой или холодного экстрагирования H_3PO_4 (pH жидкости после экстракции 2,8), чтобы удалить доступный бор.

На основании определения бора усвоенного подсолнечником установлено, что горячая экстракция водой (кипячение в течение 5 минут под обратным холодильником и промывка холодной водой) удаляет из минеральной почвы почти весь бор доступный для растений. Горячая экстракция водой почвы с высоким содержанием органического вещества не дает точного определения бора доступного для растений. Из органической почвы экстрагированной горячей водой было усвоено растениями большое количество бора.

В вариантах, где в кварцевый песок вносили почвы предыдуще экстрагированные H_3PO_4 и затем известкованные до исходного pH, симптомы недостатка бора обнаружились быстрее, чем на контрольных растениях, выращеваемых на чистом кварцевом песке. Однако это не было вызвано большим количеством фосфора в данных вариантах, как показал дополнительных опыт с возвращающими дозами фосфора в питательной смеси.

Бор адсорбированный на ионообменнике и на лигнине хорошо усвоивался растениями.