



INFLUENCE OF APPLIED CALCIUM-BORON RATIO ON THE SOLUBILITY OF NUTRIENT-ELEMENTS IN SOIL

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ABSTRACT

The present study was based on the hypothesis that the concentration of certain nutrients in soil solution can be used as a mirror for plant nutrients, with regard to the effect of applied Ca/B ratios in soil. Results revealed that the concentrations of phosphorus, sodium, copper and iron in soil solution were not significantly altered, while rest of the nutrient-elements significantly changed due to applied Ca/B ratios in soil. Results also indicate that almost all nutrient-elements correlated to Ca/B ratios in soil solution as well as in applied terms, though with a variable statistical significance. For example, phosphorus, iron, boron and molybdenum showed negative and rest of the nutrient-elements such as nitrogen (NH_4+NO_3), potassium, calcium, magnesium, sodium, zinc, manganese and copper showed positive correlation. Moreover, Soil pH showed a significantly negative correlation to Ca/B ratios in soil solution. The present study suggests that both Ca/B ratios either in soil solution or in applied terms are significant, in determining the nutrients response in soil-plant system and linking the plant nutrition to soil fertility.

Keywords: calcium, boron, ratio, soil solution, pH, nutrients concentration.

INTRODUCTION

Boron has close relationship with calcium in both plant and soil. Because calcium increase the boron requirement of plants due to similarity in function (Golakiya and Patel, 1988) and in soil reduces the availability of boron, perhaps due to the formation of a calcium metaborate complex (Sillanpaa, 1972). Some times this relationship is indicated by the Ca/B ratio of plant and soil. In the past a tremendous amount of work has been done on the effect of Ca-B ratio on the yield of various crops, but so far the relationship of this ratio with other plant nutrients is less well known. Some investigators observed this relationship with K and Na in rutabagas (Beauchamp and Hussain, 1974) and again with K in rice (Kumar *et al.*, 1981) crops, but not for other essential elements. These results indicate that Ca/B ratio has not only a close relation with the B status of plant and soil, but there seems to be some association with other nutrient-elements as well, although this relationship is not yet clear and not well documented in the literature. However, it appears that the investigation of the Ca/B ratio on the behaviour of other plant nutrients is significant for getting the maximum yield of crops. It was planned, before conducting plant's experiment in the green house and in the fields, it is preliminary essential to carry out an investigation only in soil under controlled environment. The nutrients behaviour may be best assessed through soil solution and can be used as a mirror for plant nutrients response. Because soil solution bathes plant roots and is the medium from which roots obtain inorganic nutrients (Adams, 1974). However, an understanding of nutrient concentration in soil solution is therefore essential, because it influence the processes of nutrient supply to the plant. Therefore, the present study was carried out to test a general hypothesis whether Ca/B ratio is significant either in applied or in soil solution terms in relation to other

nutrient-elements with the main objective, to assess the influence of applied Ca/B ratio on the solubility of nutrient-elements in soil.

MATERIALS AND METHODS

Experimental design and conditions:

An incubation experiment was conducted to investigate the effect of applied Ca/B ratio on the solubility of nutrients in soil solution, under green house conditions. The experiment was laid out in a randomised complete block design with six Ca/B ratios and replicated 3 times. Each treatment was represented by a small plastic pot containing 100g of soil. The pots were placed uncovered on the bench. The position of each pot was randomly changed once a week, to minimize the spatial variations in the green house during the experimental period. The maximum temperature was 22°C and the minimum 18°C, and around 65% relative humidity was kept. The incubated soil was initially watered around 20% of field capacity and water absorption and evaporation was determined by regularly weighing the pots. Deionised water was used whenever required for maintaining the moisture of soil. The incubated soil was thoroughly mixed with a plastic spatula once a week.

Description of the soil and pots used:

The soil used in the present experiments is known to be a boron deficient soil, collected from the Bracknell area near Reading, England. The soil is from sandy heath land, and is an unfertilized acid soil. A bulk sample of the top soil (0-20cm) was collected from different points at random in the area, after clearing the surface litter, and made a composite sample. Before conducting the incubation experiment a composite soil sample was air dried, ground and passed through a 2 mm sieve. The soil was characterized



for various physico-chemical properties by the routine standard procedures. The 7.5cm plastic pots were used in the present experiment, which were placed on saucers. Before use the pots and saucers were thoroughly washed in 3% hydrochloric acid and then with deionised water and dried in oven at 40°C. A glass wool filter paper was placed at the bottom of each pot to cover holes for preventing loss of soil.

Method of preparing Ca/B ratios and other nutrients application:

The soil samples were prepared by adding solutions of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and H_3BO_3 in different proportions, to obtain a wide range of Ca/B ratios. The ratios of the calcium to boron in each treatment were as follows: 2000:1, 1000:1, 500:1, 250:1, 125:1, 25:1, corresponding to the soil solution ratios of 1535:1, 648:1, 273:1, 165:1, 96:1, 23:1, respectively. The detail of the preparing original soil for desired Ca/B ratios for incubation experiment were as follow:- Soil contains a" mg Ca kg^{-1} and b" mg B kg^{-1} . We took 0.1 kg soil for each pot, this contains ac" mg Ca and bc" mg B. For example, to obtain the 1000:1 Ca/B ratio we need to add: d" mL of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ containing e" mg Ca L^{-1} : Total f" mg Ca (a-d), and g" mL of H_3BO_3 containing h" mg B L^{-1} : Total j" mg B (b-g). Then $ac + f/bc + j = 1000/1$. The other essential nutrient-elements were supplied in constant amounts according to the status of each nutrient in the test soil, such as N 24 mg kg^{-1} , P 40 mg kg^{-1} , K 110 mg kg^{-1} , Mg 60 mg kg^{-1} , Zn 1.20 mg kg^{-1} , Cu 0.56 mg kg^{-1} , Fe 0.20 mg kg^{-1} , Mn 2.40 mg kg^{-1} and Mo 0.08 mg kg^{-1} . For all nutrients application laboratory grade reagents were used.

Soil analysis:

At termination of the experiment after 48 days fresh soil from each treatment pot was collected. The soil solution from the incubated soil was extracted using the centrifugal drainage method as suggested by Kinniburgh and Miles (1983), and then subjected to elemental analysis for $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ by Technicon Auto Analyser. While, P, K, Ca, Mg, Na, Zn, Cu, Fe, Mn, Mo, B and Al concentrations were determined by ICP-OES. A brief description of the soil solution extraction procedure is presented below. At termination the pH of the incubated soil from each treatment pot was also determined on air dry basis (1:2 soil : water), to see any pH changes due to the addition of varying Ca/B in soil.

Soil solution extraction procedure:

Approximately 100g of soil was placed in the centrifuge assembly to bring the total weight up to $420 \pm 0.05\text{g}$. Four assemblies were placed in the 4 x 200 mL swing out rotor, which was spun at 6000 rpm at 5°C for one hour. The assemblies were tightly fitted in the cups and removed when the cups were cooled. Each assembly was kept vertically and the basal cup unscrewed. Solution was removed by pipette and then weighed, filtered and stored at 4°C for a short time until analysis.

Statistical analysis:

Correlation coefficients (r) were performed with the results obtained for various nutrient elements in soil solution. In addition, the data were analysed by (ANOVA) method using a computer statistical package MSTAT-C and the means were compared by LSD-test of significance (Steel and Torrie, 1980).

RESULTS

Results showed that the experimental soil was loamy sand in nature, acidic in reaction, having adequate organic matter, and deficient in mineral nitrogen, available phosphorus, potassium, molybdenum and hot water soluble-boron (Table-1).

Table-1. Physico-chemical properties of experimental soil.

Properties	Units	Values
Clay	%	4.20
Silt	%	11.4
Sand	%	84.4
Texture	-	Loamy sand
pH (1:2)s	-	4.93
CEC	cmolc kg^{-1}	4.94
Base saturation	%	45.1
Organic matter	%	4.14
Available $\text{NO}_3 - \text{N}$	mg kg^{-1}	0.13
" $\text{NH}_4 - \text{N}$	"	0.40
" P	"	3.36
" K	"	25.0
" Ca	"	125
" Mg	"	7.60
" Na	"	10.0
" Zn	$\mu\text{g g}^{-1}$	4.20
" Cu	"	1.54
" Fe	"	5.13
" Mn	"	5.00
" Mo	"	0.03
" B	"	0.44

Nutrients concentration in soil solution:

Nitrogen:

The results of $\text{NH}_4\text{-N}$ showed a decreasing trend with decreasing the Ca/B ratios in soil, while $\text{NO}_3\text{-N}$ showed an increasing trend up to the applied Ca/B ratio of 250:1 or soil solution ratio of 165:1 (Table-2) and onward decreased. The combined concentration of nitrogen (total inorganic N) resulted in a positive correlation with both Ca/B ratios in soil solution or in applied terms (Table-3). As it is evident from the data, the results of total inorganic N is not very consistent, however LSD-test show significant differences among the treatments of both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ due to varying Ca/B ratios, therefore under the conditions of the experiment it is difficult to say whether the decrease/increase of N was due to the effect of Ca/B ratios or soil pH.

**Table-2.** Influence of Ca/B ratios on the concentration of nutrient-elements in soil solution.

Ca/B Ratio Applied soil solution		NH ₄ N	NO ₃ N	P	K	Ca	Mg	Na	Zn	Cu	Fe	Mn	Mo	B	Al
		----- mg L ⁻¹ -----													
2000:1	1535:1	103.1	1.73	0.83	429.2	2601.3	154.51	21.92	3.84	0.02	0.12	20.17	0.05	1.70	3.27
1000:1	648:1	88.69	3.25	0.96	394.4	1224.7	135.09	21.06	2.16	0.02	0.13	13.97	0.05	1.89	1.87
500:1	273:1	74.65	14.0	1.12	331.7	542.64	103.25	20.97	1.22	0.02	0.14	8.20	0.06	1.99	1.62
250:1	165:1	57.77	35.8	1.39	293.4	336.10	83.05	18.95	0.99	0.01	0.20	5.93	0.08	2.04	1.30
125:1	96:1	52.12	8.46	1.40	279.9	283.62	77.10	20.72	0.78	0.01	0.50	5.60	0.15	2.94	1.11
25:1	23:1	72.50	2.39	1.33	280.4	268.18	75.50	20.42	0.73	0.01	0.27	5.23	0.19	11.8	1.07
LSD(P<0.05)*		14.83	1.45	NS	28.29	152.90	9.59	NS	0.15	NS	NS	1.71	0.02	0.25	NS
LSD(P<0.01)**		23.26	2.28	NS	44.37	239.80	15.0	NS	0.23	NS	NS	2.68	0.03	0.39	NS

* , ** = indicate significant (P < 0.05) and (P < 0.01), respectively.

NS = Non-significant

**Phosphorus:**

Results show as the Ca/B ratio in soil decreases the concentration of phosphorus in soil solution increases (Table-2) and resulted in a significantly negative correlation with both in soil solution and applied (Table-3). Although phosphorus increases but the differences found among the treatments were statistically non-significant. Results further show that a small depression occurred in the phosphorus concentration at highest Ca/B ratio in soil, which may be due to the interaction of phosphorus with other elements in soil.

Potassium:

The results of potassium are in contrast to phosphorus. It is evident from the data and LSD-test that the concentration of potassium in soil solution significantly decreases as the Ca/B ratios decreased (Table-2), which resulted significantly positive relationship with both in soil solution and applied (Table-3). This was presumably due to simple ion exchange processes, calcium displace potassium in soil.

Calcium:

As could be expected the concentration of calcium in soil solution decreases as the Ca/B ratios in soil decreases (Table-2) and resulted in a close positive correlation (Table-3). A similar close relationship was found with applied Ca/B ratios in soil. This confirms the relationship between calcium and boron with regard to Ca/B ratios in soil and also an agreement with the literature (Golakiya and Patel, 1980 and Su *et al.*, 1994). Results also show differences found in the soil solution calcium were statistically significant due to large variation in the applied ratios.

Magnesium:

Magnesium followed the trend of potassium, suggesting that as the Ca/B ratio in the soil decreases the concentration of magnesium in soil solution significantly decreases as well (Table-2), which resulted in a positive correlation with both in soil solution and applied (Table-3). This similarity indicates that the activities of cations such as K^+ , Mg^{++} and Na^+ increased where soil pH decreased. These results are in agreement with work of Curtin and Smillie (1983) who reported that the activities of the major cations (K^+ , Ca^{++} , Mg^{++} and Na^+) increased substantially when pH decreased during incubation.

Sodium:

Similarly sodium also followed the trend of other basic cations, but non-significant differences were found among the various treatments (Table-2), and showed positive correlation with Ca/B ratios in soil solution and with applied (Table-3). Results also show that the concentration of sodium is more reduced when the soil receiving a Ca/B ratio of 250:1, corresponding to soil solution ratio 165:1, however this reduction may be due to the complex interactions among cations (K^+ , Ca^{++} , Mg^{++} and Na^+) in soil.

Zinc:

It is evident from the results that with decreasing the Ca/B ratios in soil the concentration of zinc in soil solution significantly decreases (Table-2), which resulted significantly positive correlation with soil solution and with applied ratios (Table-3). The maximum zinc concentration was obtained at the highest Ca/B ratio in soil, suggesting close similarity with the other basic cations. The explanation for this similarity may be due to the lower pH at higher Ca/B ratios, and perhaps basic cations were displaced from exchange sites by protons, and more zinc was released into solution. These results are in line with the results of Curtin and Smillie (1983).

Copper:

Results regarding the concentration of copper in soil solution are irregular (Table-2), although copper did show a positive correlation with Ca/B ratios in soil solution and with applied (Table-3), but statistically it is non-significant in both cases. Results further show that there is no considerable effect of Ca/B ratio on the availability of copper in soil solution, suggesting perhaps organic matter depressed its availability which could not much release into solution (Cox and Kamprath, 1972; Tisdale *et al.*, 1985). The latter authors reported that the concentration of copper in soil solution is usually found in the range of 0.0006 to 0.063 mg L^{-1} .

Iron:

The results for iron are somewhat similar to phosphorus (Table-2). Results shows with decreasing the Ca/B ratios the concentration of iron in soil solution increases and then decrease at the lowest ratio. However, negative and non-significant correlations were found between Ca/B ratio in soil solution and with applied (Table-3). The explanation for reduced iron availability at lowest Ca/B ratio (applied 25:1 or in soil solution 23:1) presumably due to increase soil pH (Katyal and Randhawa, 1983), or imbalance ratios with other cationic micronutrients (Tisdale *et al.*, 1985).

Manganese:

Results showed the concentration of manganese significantly decreases with decreasing the Ca/B ratios in soil solution (Table-2), and resulted significantly positive correlation both in soil solution and applied (Table-3). Like zinc the maximum and minimum manganese concentrations were found at highest and lowest Ca/B ratios in soil solution, and almost similar explanation can be offered for the present situation. However, as mentioned earlier the concentrations of major cations (K^+ , Mg^{++} , Na^+ and NH_4^+) increased substantially, whereas pH decreased, and presumably the decline in pH was accompanied by increase in Al^{+++} , Zn^{++} and Mn^{++} , in soil solution, because the concentrations of Al^{+++} , Zn^{++} and Mn^{++} showed close correlation to soil pH (Curtin and Smillie, 1983). The explanation for such evidence is that the more manganese was present in the soil



solution due to low pH or high aluminium content in soil, because of total acidity.

Molybdenum:

Results showed as the Ca/B ratios in soil decreases the concentration of molybdenum in soil solution increases (Table-2), which resulted in a negative and non-significant correlation with both in soil solution and applied (Table-3). Further, LSD-test show that no significant changes occurred in the solution molybdenum when the soil received Ca/B ratios from 2000:1 to 250:1. The present results suggest that all anions such as phosphorus, boron, molybdenum and to some extent NO_3 -nitrogen increase when the levels of boron in soil increased. However, the similarity found in the trends of the anions concentrations may be due the effect of soil pH

or some other factors other than pH involved under the conditions of the experiment.

Boron:

Again as expected, the concentration of boron increases with decreasing the Ca/B ratios in soil solution (Table-2), which resulted non-significant and negative correlation with both in soil solution and applied (Table-3). The data clearly showed that boron was not released into solution where high levels of calcium were applied to soil, while the reverse situation found at lower levels of calcium. This again suggests the negative relationship between boron and calcium in soil due to interactions. These results are in line with the previous work of Golakiya and Patel (1980) and Su *et al.*, (1994).

Table-3. Correlation coefficients (r) between nutrients concentrations in soil solution and Ca/B ratios.

Elements	r = (Soil solution ratio)	r = (Applied ratio)
N ($\text{NH}_4 + \text{NO}_3$)	0.73 *	0.76 *
P	-0.89**	-0.93**
K	0.93**	0.96**
Ca	0.99**	0.99**
Mg	0.94**	0.96**
Na	0.70 *	0.71 *
Zn	0.99**	0.99**
Cu	0.69 NS	0.76*
Fe	-0.55NS	-0.60 NS
Mn	0.98**	0.99**
Mo	-0.63 NS	-0.69 NS
B	-0.43 NS	-0.48 NS

* , ** = indicate significant ($P < 0.05$) and ($P < 0.01$), respectively

NS = Non-significant

Ca/B Ratio:

In the present study, the calcium-boron ratio of the soil solution was plotted against the applied ratio, to see the relationships between applied and soil solution ratios. Figure-2 shows as the applied ratio decreases simultaneously soil solution ratio is significantly decreased, and resulted in a positive correlation ($r = +0.99$). Similar results were reported by Golakiya and Patel (1988). These results indicate that both applied and soil solution ratios run parallel, and soil solution ratio can be used as a mirror of the total (applied + native) ratio. Although the relationship is not very linear but the r-value indicates that the solution ratio is dependent on the applied ratio in soil. Results further suggests that the possibility of using Ca/B ratio in soil as a guide in determining the need of boron fertilization, which also seems

to be a good indicator for crop response to boron fertilization in low and high calcium soils.

Soil pH:

It is important to see the behaviour of soil pH along with the results of nutrients concentration in soil solution, because the nutrient availabilities are dependent on pH. Results showed as the Ca/B ratios in soil solution decreases the pH of soil increases (Figure-1), and resulted in a significantly negative correlation with both Ca/B ratios in soil solution ($r = -0.92$) and applied ($r = -0.95$). The possible explanation for increase pH with decreasing Ca/B ratios was due to the release of cations into solution perhaps due to liberation of protons along with NO_3^- as a result of organic matter mineralization. Basic cations were displaced from exchange sites by protons, Al^{+3} , Mn^{+2} increases (Table-3) and pH of the soil decreased (Curtin and Smillie, 1983).

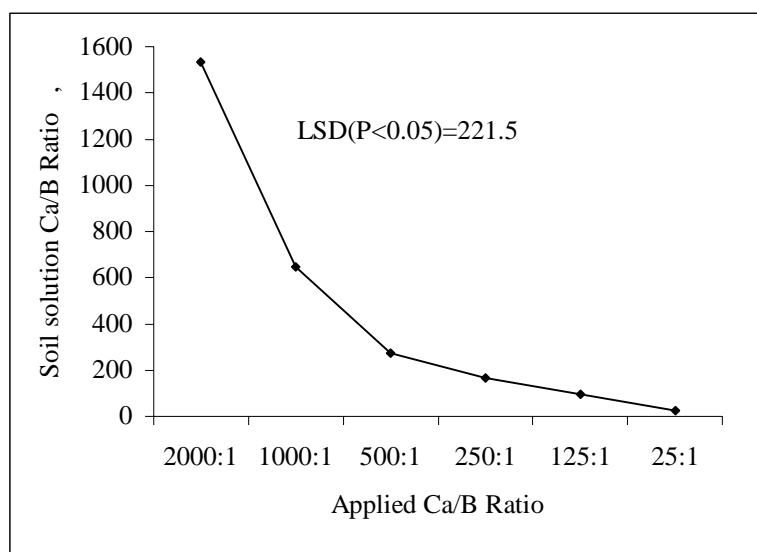


Figure-1. Relationship between applied and soil solution Ca/B Ratio.

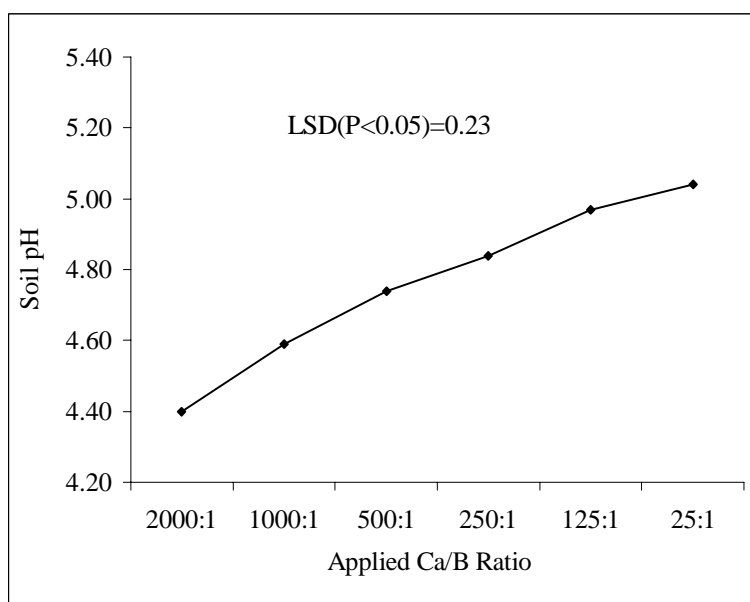


Figure-2. Relationship between Ca/B Ratio and soil pH.

DISCUSSION

The main aim of the present investigation was to see the nutrient behaviour in soil solution with regard to the effect of both Ca/B ratios in soil solution as well as applied, before initiation of the plant's experiment. However, the results suggests there is a relationship between the Ca/B ratios and other nutrients in soil solution, but the elements relationship depended on the degree of statistical significance, and it can be expect that the same trends of the various nutrients may be occurred in plants, because plant nutrients are generally depends on the availability of the respective nutrients in soil solution. In the present study no traditional extractants were used for the determination of available status of nutrients, the nutrients concentration were directly determined in soil solution, because it influences the processes of nutrient supply to the plant. Therefore,

knowledge of soil solution characteristics is also valuable in making predictions of plant response to the chemical environment. Soil solution chemistry may therefore, provide a valid measure of the nutrient status of a soil (Campbell *et al.*, 1989). However, it was noted from the results of the present study that phosphorus, iron, molybdenum and boron showed negative and rest of elements such as nitrogen (NH_4+NO_3), calcium, magnesium, sodium, zinc, copper and manganese showed positive correlation to Ca/B ratios in soil. Moreover, the nutrient-elements were grouped according to their response to Ca/B ratios either with soil solution or with applied e.g., potassium, calcium, magnesium, sodium, zinc and manganese showed decreasing trend, and phosphorus, iron, molybdenum and boron showed an increasing trend, whereas nitrogen and copper showed irregular trends. Furthermore, soil pH also showed significantly negative



correlation to Ca/B ratios in soil solution. It was also found that phosphorus, iron, molybdenum and boron showed positive and rest of the ions have negative relationship to soil pH. The present study and those who worked on plants regarding the plant nutrients response to Ca/B ratio (Beauchamp and Hussain, 1974; Kumar *et al.*, 1981), provided the knowledge of linking the plant nutrition to soil fertility. The information obtained from the present study could directly be applicable to field conditions, specifically in calcareous soils where boron availability is one of the main problems (Patel and Golakiya, 1986) and fertilization of boron is necessary for high demanding crops, or in strongly acid sandy soils where liming is a common practice (Su *et al.*, 1994) and boron is one of the limiting nutrient on these soils, or in saline-sodic soils (Lal *et al.*, 1979) where boron toxicity is main problem and gypsum (calcium sulphate) always used to ameliorate the soils. On such soils perhaps both calcium-boron have regulatory or inhibitory influence on the availability of other nutrient-elements to plants. Therefore, the knowledge of balance ratio between calcium and boron in fertilizer, in soil, and in plant and subsequent effect on the other nutrients availability is utmost important for obtaining a maximum yield of crops. However, future research is required in the improvement of the present study to investigate what kinds of physiological and chemical factors affect the availability of nutrients to plants with regard to calcium-boron ratio in soil.

CONCLUSION

The following conclusions were drawn from the present incubation study:

- Results revealed that the concentrations of phosphorus, sodium, copper and iron were not significantly altered, while rest of the nutrient-elements significantly changed due to applied Ca/B ratios in soil. Results also indicated that almost all nutrient-elements correlated to Ca/B ratios either in soil solution or applied, though with a variable statistical significance. For example, phosphorus, iron, boron and molybdenum showed negative and the rest of the nutrient elements such as nitrogen (NH_4+NO_3), potassium, calcium, magnesium, sodium, zinc, manganese and copper showed positive correlation.
- Soil pH also showed significantly negative correlation to Ca/B ratios in soil solution. Moreover, it was found that the ions such as phosphorus, iron, boron and molybdenum have positive, and the rest of the ions have a negative relationship to soil pH.

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