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Effect of varying calcium carbonate content on Boron availability in Loamy Sand Soil of Punjab

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Abstract
A laboratory experiment was conducted to estimate the effect of incubated time on release of boron (B) from loamy sand soil, containing varying levels of calcium carbonate. Different levels of calcium Carbonate (0, 2.5, 5.0 and 10% powdered) and boron (0, 1.25, 2.5, 5.0, 10.0 mg B kg^{-1} soil) were applied to soil in completely randomized design with three replications and soil was incubated at 25°±1°C. At weekly intervals, the soil was thoroughly mixed and subsample was removed after 0, 7, 14, 28 and 56 days incubation for analysis. The results showed availability of boron was maximum treatment having no calcium carbonate (B_0C_0, $B_{1.25}C_0$, $B_{2.5}C_0$, $B_{5.0}C_0$ and $B_{10.0}C_0$) content. However, the availability of boron decreased with increase in calcium carbonate content and with passing time (7, 14, 28 and 56 days). Availability of boron was least in the presence of highest calcium carbonate (B_0C_{10}, $B_{1.25}C_{10}$, $B_{2.5}C_{10}$, $B_{5.0}C_{10}$ and $B_{10.0}C_{10}$) content. From this study, it was concluded that concentration of boron was decreased with increasing calcium carbonate content and time. Calcium carbonate showed a negative effect on boron availability.

Keywords: Boron, calcium carbonate, loamy sand soil, incubation

Introduction

Boron (B) is an essential micronutrient required for growth and yield of crops due to its major role in formation, maintenance of cell wall and cell membrane integrity. According to Nadian *et al*. (2010) [19] insufficient micronutrients like boron are often common. Hence, these elements can be supplied as fertilizers in both intensive and extensive agriculture, particularly in calcareous soils. Boron deficiency is common in sandy and highly calcareous rich soils due to interaction between the calcium ions and available B content. Also, the presence of high calcium levels at high pH reduces B availability (Marschner 1995) [17]. Singh and Nayyar (1999) [26] reported that boron deficiency occurred in crop plants grown on light textured sandy calcareous soils. Calcium carbonate acts as an important B adsorbing surface in calcareous soils (Elseewi 1974) [3]. Calcium carbonate was non-significantly correlated with water soluble boron content of soils. However, Paliwal and Mehta (1973) [21] reported that in the soils of Kota and Bhilwara regions of Rajasthan, availability of water soluble B was negatively related to the calcium carbonate content.

Crops grown on limed acid soils generally showed sensitivity to B deficiency and manifest its visual symptoms of deficiency due to adsorption of B by lime (Scoot *et al*. 1975). In addition to the indirect effect of calcium carbonate on boron adsorption, co-precipitation of boron with calcium carbonate may have also occurred (Kitano *et al*. 1978) [13]. Earlier, reduced availability of B following liming has been ascribed to the formation of boric acid esters with higher alcohols. Sims and Bingham (1968) [25] threw considerable light on the nature of B retention and the better understanding of the reactions involved in B fixation. The adsorption of B on Al-hydroxide was studied by Hatcher *et al*. (1967) [11]. They reported that freshly precipitated Al(OH)3 absorbed large quantities of boron while adsorption decreased markedly with time. The reaction between exchangeable Al and lime may be summarized as follows:

$$2AlX_3 + 3CaCO_3 + 3H_2O = 3CaX_2 + 2Al(OH)_3 + 3CO_2$$

Where, X is the exchange site, the freshly precipitated $Al(OH)_3$ is then available for adsorption of B. $CaCO_3$ content of the salt affected soils of Punjab was found to be significantly correlated with the available and total boron.

Goldberg (1997) [5] observed that lime (calcium carbonate) was one of the most important factors affecting the adsorption of B. Marschner (1986) [16] indicated that in soils with high pH, lime and clay content, plant available B reduced by the formation of $B(OH)_4$ and adsorption of anions. In general Ca^{2+}/B ratio is a good indicator of the B status of the plant (Blamey *et al*. 1979) [1]. Increasing Ca^{2+}/B ratio resulted in B deficiency. Tariq and Mott (2006) [28]. observed that Ca^{2+}/B ratio in the soil solution had a negative relationship with phosphorus, iron, boron, molybdenum, while it had a positive relationship with nitrogen, potassium, calcium, magnesium, sodium, zinc, manganese and copper. Application of lime increases B fixation by soils because it raises the soil solution pH (Elseewi 1974; Elseewi and Elmalky 1979) [3-4]. In addition to its effect on the soil pH, calcium carbonate also acts as an important B adsorbing surface in calcareous soils (Goldberg and Forster 1991) [7]. Retention of B on calcium carbonate occurs through as adsorption mechanism. The mechanism could be the exchange with carbonate groups. The magnitudes of the B adsorption maxima for soil samples treated to remove calcium carbonate were statically significantly lower than those for untreated soil samples indicating that calcium carbonate acts as an important sink for B adsorption in calcareous soils (Goldberg and Forester 1991) [7]. The objective of our experiment was to study the effect of varying calcium carbonate content on boron availability.

Material and Methods

The experiment was conducted in the laboratory of the department of soils in Punjab agricultural university, Ludhiana. The study area is situated in the Centre of Punjab state, which was not recently limed and fertilized with B fertilizer. Chemical and physical properties of the soil are given in Table 1.

Table 1: Physico-chemical characteristics of the experiment field soil before sowing

Characteristics	Contents
*pH (1:2)	7.5
*EC(dS m^{-1})	0.43
Organic carbon (%)	0.35
Mechanical composition	
Sand (%)	72.4
Silt (%)	16.0
Clay (%)	11.6
Texture	Loamy sand
$CaCO_3$ (%)	Nil
DTPA extractable (mg kg^{-1} soil)	
Zn	0.54
Mn	6.86
Fe	10.5
Cu	0.88
Hot water soluble boron (mg B kg^{-1} soil)	0.42

*(1:2, Soil: Water suspension)

Incubation study

A laboratory experiment was conducted to study the effect of varying calcium carbonate content on boron availability in loamy sand soil. Polythene-lined plastic pots were filled with 2.0 kg of soil. Thereafter, treatments consisting of four levels of calcium carbonate (0, 2.5, 5.0, 10% powdered) and five levels of B as borax (0, 1.25, 2.5, 5.0, 10.0 mg B kg^{-1} soil) were imposed on soil, which were tested in a completely randomized design (CRD) with three replications. Calcium carbonate and B were added to soil in pots and left under incubation for completion of the reaction, with seven days interval mixing, were kept for 56 days at field capacity. Available B (hot-water extractable) content of the soil was estimated at 0, 7, 14, 28 and 56 days of imposition of treatments of calcium carbonate and B.

Analysis of boron in soil

Hot water soluble boron was determined by the method described by Wear (1965) [29]. Ten-gram soil was taken in 250 ml flask and then 20 ml deionized water and 0.2 gram of activated charcoal was added into the flask and reflux condenser was attached to the flask. The flask was heated on the hot plate to the first sign of boiling, followed by refluxing of the contents for 5 minutes. Contents were allowed to cool and filtered through Whatman No. 42 filter paper. Boron in the soil was estimated colorimetrically using azomethine-H method given by Shania *et al.* (1967) and later on modified by Gupta (1967) [11]. Briefly, one ml of extract was taken into a 10 ml polypropylene tube. To this, 2 ml of buffer (EDTA-sodium salt) and 2 ml of azomethine-H solution were added. The content was mixed thoroughly by inverting the tube and was allowed to stand for half an hour. The intensity of the colour was measured on a spectrophotometer at the wavelength of 420 nm. The amount of boron in the extract was calculated from the standard curve prepared by taking standard solutions containing 0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0 ppm boron.

Boron availability with time by using simple first-order kinetic equation

The simple first order kinetic equation is

$$\ln C_t = \ln C_0 - kt$$

C_t (µg g^{-1}) was the residue concentration at time t, C_0 (µg g^{-1}) is an initial concentration after application (t = 0), t is time after boron and calcium carbonate application and k ($days^{-1}$) was the dissipation rate constant, which was calculated from slope by plotting $\ln C_t$ *vs.* t (days).

Statistical analysis

The statistical analysis of the data was done using a completely randomized design (factorial) and critical difference (CD) computed at the 5 per cent probability level (Gomez and Gomez 1984).

Results and Discussion

Our incubation study resulted; the availability of boron was decreased as a function of time and with varying calcium carbonates treatments for soil. In the incubation study, availability of boron after 0, 7, 14, 28 and 56 days were represented in figures (1, 2, 3, 4, and 5). This is probably because boron reacts with calcium carbonate and form sparingly soluble calcium borates complex, substitution of B for carbon in mineral structure and boron adsorbed on the surface of calcium carbonate. Calcium carbonate content of soil increased B fixation because it raised the soil solution pH. Boron desorption generally decreased as a function of time for each extraction and for all of the treatments. This result indicated that calcium carbonate acts as an important sink for boron sorption in calcareous soils. Calcium carbonate had the negative effect on boron availability. As from, its effect on soil pH, calcium carbonate also played an important role as a B adsorbing surface in calcareous soils (Elseewi 1974; Elseewi and Elmalky 1979; Goldberg and Forster 1991) [3, 4, 7]. Olsen and Berger (1946) [20]; Kubota *et al* (1948) [14] found that increasing the alkalinity of a soil increased adsorption thereby reducing leaching, but did not rendering B unavailable for extraction by the hot water method. Although a number of workers had reported a decreased availability of B with calcium carbonate.

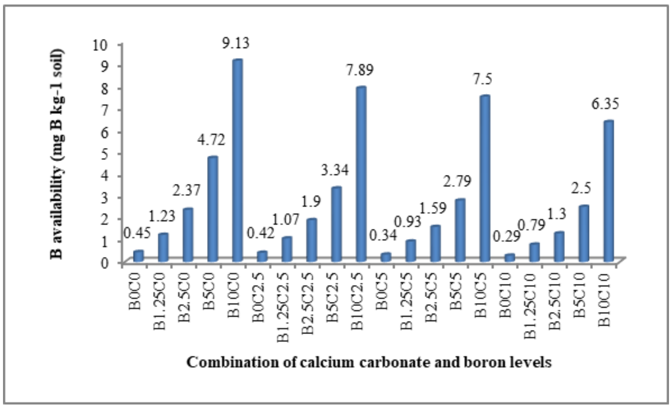

Fig 1: Effect of varying calcium carbonate content on boron availability after zero day incubation

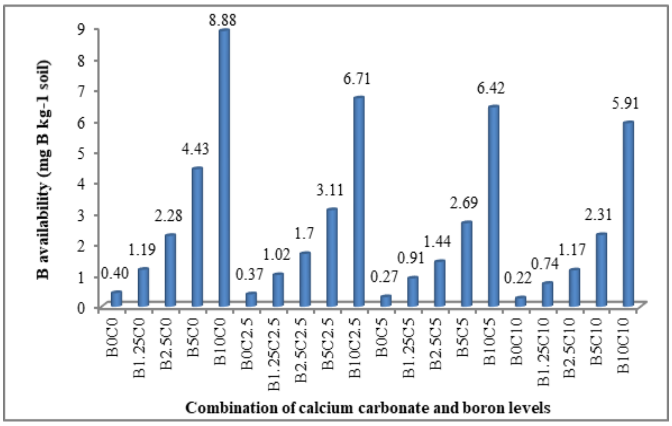

Fig 2: Effect of varying calcium carbonate content on boron availability after seven days incubation

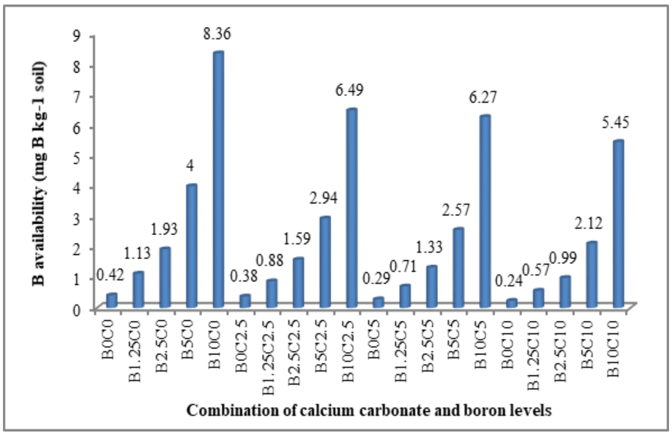

Fig 3: Effect of varying calcium carbonate content on boron availability after fourteen days incubation

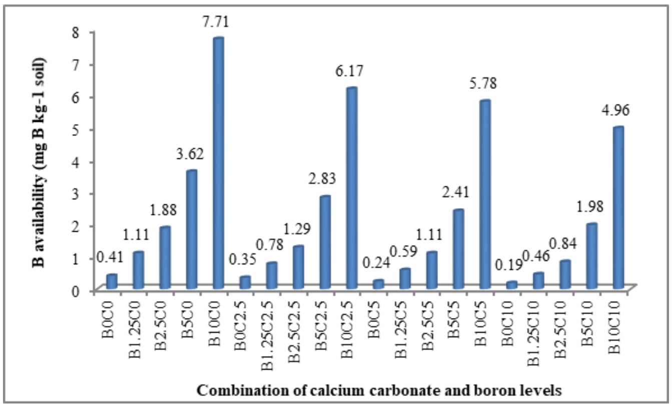

Fig 4: Effect of varying calcium carbonate content on boron availability after twenty-eight days incubation

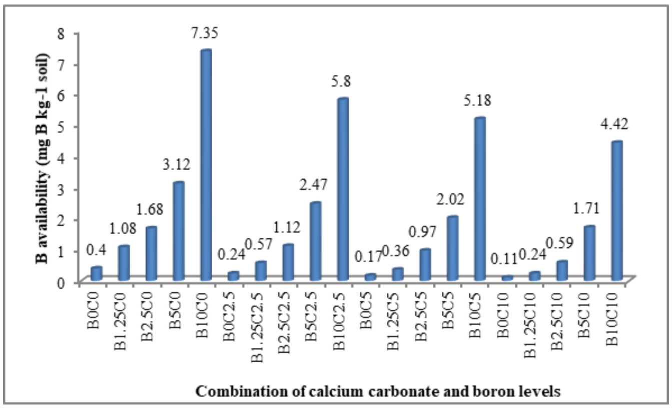

Fig 5: Effect of varying calcium carbonate content on boron availability after fifty-six days incubation

To study the effect of varying calcium carbonate content on boron availability with time simple first-order kinetic equation (SFOK) was applied. The available concentration of boron plotted against the time a decreasing slope of the line was obtained, represented in the figures (6, 7, 8 and 9). The decreasing slope of the line was indicated that availability of boron decreased in different treatments with time. The availability of boron was more where calcium carbonate was not appliedand it decreased further with increase in concentration of calcium carbonate (figure 6, 7, 8 and 9).

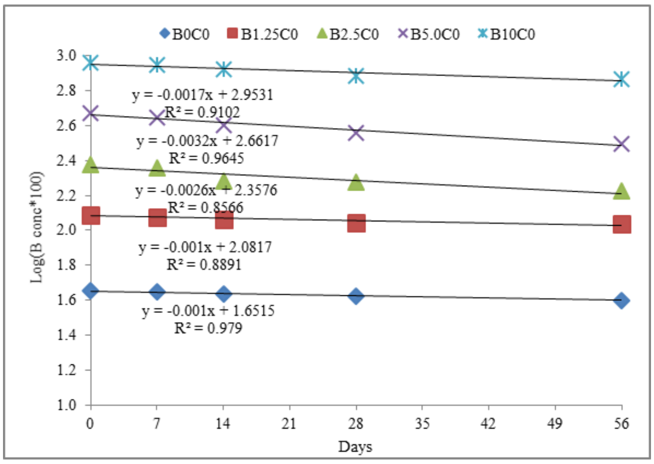

Fig 6: Availability of boron with time, when different levels of boron (B_0, $B_{1.25}$, $B_{2.5}$, $B_{5.0}$ and $B_{10.0}$ mg B kg^{-1} soil) were applied with zero per cent of calcium carbonate (C_0).

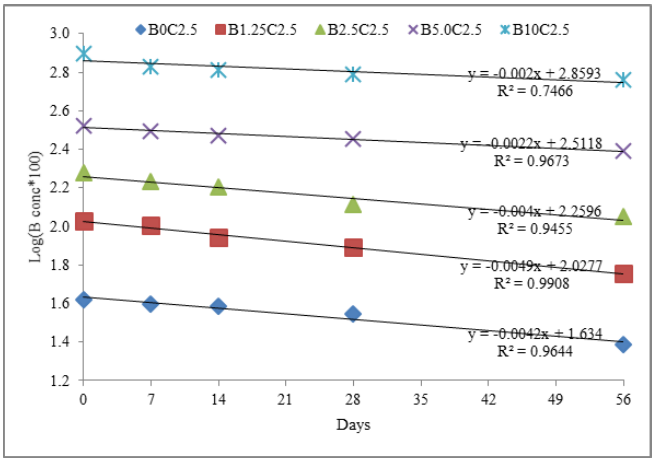

Fig 7: Availability of boron with time, when different levels of boron (B_0, $B_{1.25}$, $B_{2.5}$, $B_{5.0}$ and $B_{10.0}$ mg B kg^{-1} soil) were applied with 2.5 per cent of calcium carbonate ($C_{2.5}$).

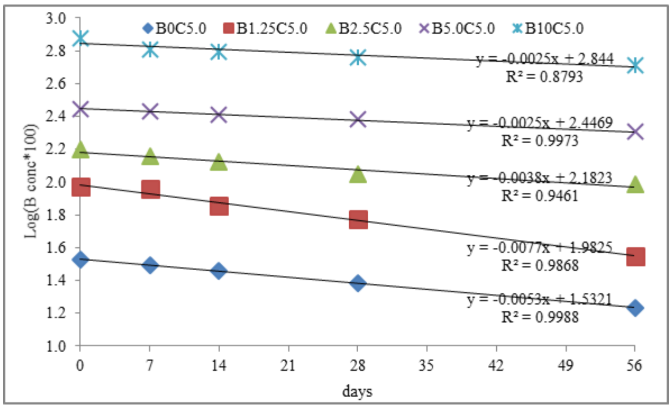

Fig 8: Availability of boron with time, when different levels of boron (B_0, $B_{1.25}$, $B_{2.5}$, $B_{5.0}$ and $B_{10.0}$ mg B kg^{-1} soil) were applied with 5.0 per cent calcium carbonate ($C_{5.0}$).

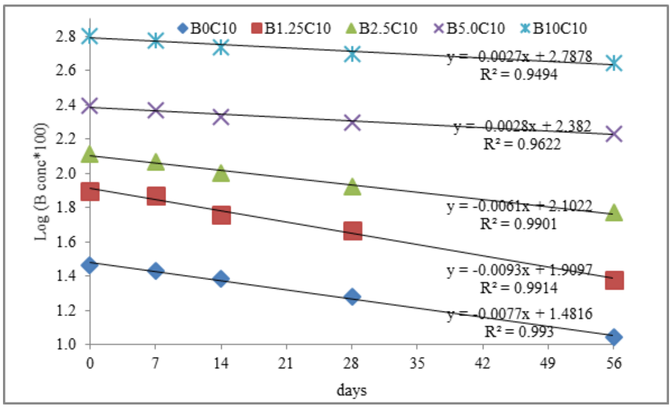

Fig 9: Availability of boron with time, when different levels of boron (B_0, $B_{1.25}$, $B_{2.5}$, $B_{5.0}$ and $B_{10.0}$ mg B kg^{-1} soil) were applied with 10 per cent calcium carbonate (C_{10}).

Goldberg and Suarez (2011) [6] reported that the decrease in B release with respect to incubation time approached zero for all five soils for most of the extractant solutions. Because the decrease in extractable B with time for four of the soils was significant, a very good indication of extractable soil B could be obtained from a one-month incubation study. With time, availability of boron started decreasing because boron started to adsorbed on the surface of calcium carbonate and made the insoluble complex (calcium-mono-borate complex) due to this reason availability of boron decreased with increasing the level of calcium carbonate.

Soil solution B concentrations were controlled by adsorption-desorption reactions, released from tetrahedral sites of clay minerals and amorphous alumina-silicate phases, or dissolution of B-containing minerals (Su and Suarez 2004) [27]. It was generally assumed that B adsorption and desorption reactions occur virtually instantaneously and reversibly so that B adsorption results could be used to describe B desorption behavior. This was indeed the case for some soils, where the B desorption isotherm closely corresponded to the adsorption isotherm (Hatcher and Bower 1958; Elrashidi and O'Connor 1982) [12, 2].

The rate of B desorption from soils was found to decrease over time after initial B addition and was attributed to B diffusion out of the interior of clay mineral particles (Griffin and Burau 1974) [9]. Boron fixation by the clay minerals kaolinite and smectite increased as incubation time was increased from 1 to 4 weeks (Parks and White 1952) [22]. Boron retention in a Norwegian forest soil doubled on incubation for 8 weeks from that obtained after 17 hours (Letho 1995) [15]. Up to 82 per cent of B applied to Fresh soils was fixed to hot-water extraction after 100 days of incubation, as opposed to 49 per cent after 20 hours (Saarela 1985) [24]. It had been suggested that native adsorbed B was held with greater tenacity in soils than B that had been artificially added (Rhoades *et al* 1970) [23].

The majority of recent studies had reported an antagonistic relationship between boron and calcium (Ca^{2+}) concentrations at plant-soil interface. The major soil properties like pH, texture, lime, moisture, temperature, organic matter and clay mineralogy had largest effects on available B in the soil (Goldberg 1997) [5]. The author reported that lime (calcium carbonate, $CaCO_3$) was one of the most important factors affecting the adsorption of boron. Marschner (1997) [18] indicated that in soils with high pH, lime and clay content, plant available boron was reduced by the formation of $B(OH)_4$ and adsorption of anions.

Conclusion

From our study, we concluded that availability of boron was decreased with applied different levels of calcium carbonates for each extraction and as function of time. This may be due to boron reacts with calcium carbonate and form sparingly soluble calcium borates complex, substitution of B for carbon in mineral structure and boron adsorbed on the surface of calcium carbonate. Liming of soils increases B fixation because it raises the soil solution pH. Available concentration of boron was plotted against the time; a decreasing slope of the line was obtained. The decreasing slope of the line indicated that availability of boron was decreased with time. Availability of boron was highest after zero days and no calcium carbonate (C_0) level was applied and lowest after fifty-six days and at calcium carbonate level applied. Availability of boron was highest with no calcium carbonate was applied. Further, an increase in the level of calcium carbonate the availability of boron was decreased. This result indicates that calcium carbonate acts as an important sink for boron sorption in soils. Calcium carbonate has a negative effect on boron availability.

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