

## CROPS AND SOILS REVIEW

# Fractions of soil boron: a review

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### SUMMARY

Knowledge of different fractions and availability of boron (B) is essential while studying the response of crops to B. Fractionation provides information about the chemistry of B and quantifies its bioavailability. Such information is potentially valuable for predicting bioavailability, B leaching, dynamics, transformation between chemical forms in soils and environmental impacts. Total B (T-B) is quantified into five fractions: readily soluble (Rs-B), specifically adsorbed (Spa-B), oxide bound (Ox-B), organically bound (Org-B) and residual B (Res-B). Of these, Rs-B is the fraction present in soil solution and adsorbed weakly by soil particles, and is most readily available for plant uptake. It accounts for 1–2% of T-B. The second most plant available form is Spa-B; it may be adsorbed onto clay surfaces or associated with organic matter (OM) in soil. The remaining fractions, Ox-B, Org-B and Res-B, are unavailable for plant uptake. The major portion (generally 87.4–99.7%) of T-B is composed of Res-B. Overall, the relative proportion of B in various fractions is in the order of Res B > Org-B > Spa-B > Rs-B > Ox-B. Several factors such as soil pH, soil OM, clay minerals, iron and aluminium oxides and calcium carbonate content may change the relative proportion of B in various fractions and the transformations among different soil B fractions. Some of the B fractions are correlated with others and exhibit responses in terms of plant growth. Non-specifically adsorbed (Nsa-B) and Spa-B are positively and significantly correlated to some sub-fractions of Ox-B, such as B occluded in manganese oxyhydroxides (Moh-B). The most readily available forms of B for plants are Nsa-B, Spa-B and Moh-B.

### INTRODUCTION

Boron (B) is an essential trace element, with a narrow range between its phytotoxic limit and the deficient level in the soil (Reisenauer *et al.* 1973). This range depends on the soil type, total B content and age of the plant. Boron plays an important role in flowering and fertilization processes, and in boosting yield and quality of crop produce (Kanwar & Randhawa 1974). It can be one of the main limiting micronutrients in coarse textured, sandy calcareous soils. It is retained in soils by adsorption onto mineral and humic particles and by forming insoluble precipitates (Couch & Grim 1968; Goldberg & Glaubig 1985). Boron deficiency can be a major constraint to crop production (Sillanpaa 1982), and has been reported in more than 80 countries and for at least 132 crops over the last

70 years (Shorrocks 1997). The deficiency of B has been realized as the second most important micronutrient constraint in crops after that of zinc (Zn) on a global scale. Sillanpaa (1990) acknowledged that 21% of soils in research investigations conducted worldwide across 14 countries were B deficient. In India, B deficiency affects 33% of soils, particularly alluvial soils (Sakal & Singh 1995; Singh 2008). Excessive and toxic levels of soil B are reported in semi-arid and arid areas and saline soils with drainage problems (Keren & Bingham 1985). Boron is distributed in various soil components, including soil solution, organic matter (OM) and minerals. Boron in soil solution is readily available for plant uptake, but maintaining B in the soil solution is an important aspect for plant nutrition and it is controlled by the pools of B in other soil fractions and their equilibration with soil solution (Xu *et al.* 2001). The proportion of various B forms varies considerably, depending on soil type and

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extraction technique used (Raza *et al.* 2002). Boron in soil is considered to be distributed among several geochemical forms that include readily soluble, specifically adsorbed, oxide bound, organically bound and residual forms. The proportion of B associated with different geochemical forms depends greatly upon physico-chemical properties of soils, climate and management practices. Several soil factors such as pH, OM, clay minerals, iron (Fe) and aluminium (Al) oxides, carbonates and tillage may influence the content of extractable B and transformations among different soil B fractions (Jin *et al.* 1987; Mandal *et al.* 1993; Hou *et al.* 1994; Tsalidas *et al.* 1994; Yermiyahu *et al.* 1995). These B fractions have remarkable differences in mobility, bioavailability and chemical behaviour of soils and can be transformed under certain conditions.

Fractionation is used to identify and quantify various forms of soil B, each forming a fraction of total soil B. Such information is potentially valuable for predicting bioavailability, leaching, dynamics, transformation between various chemical forms in soils and environmental impacts (Hedley *et al.* 1982; Sui *et al.* 1999). Fractionation along with information about the chemistry of B is fundamental for understanding its chemistry in soils and the potential contribution of these fractions to plant uptake of B. Studying the forms of B present in soil provides knowledge of B status and potential supply to plants. Various researchers have quantified total soil B in terms of the following five fractions: (i) readily soluble, (ii) specifically bound, (iii) organically bound, (iv) oxide bound and (v) residual (Jin *et al.* 1987; Hou *et al.* 1994, 1996).

## FRACTIONS OF BORON

### Readily soluble boron

Among all fractions, readily soluble boron (Rs-B) is the first and most readily available form for plant uptake, which is in soil solution or weakly adsorbed by soil particles (Keren *et al.* 1985). This pool constitutes 1–2% of total soil B (Jin *et al.* 1987; Tsalidas *et al.* 1994). Padbhushan & Kumar (2015a) reported Rs-B forms to be <1% of total B in alkaline calcareous soils of Punjab, India (Table 1). This fraction decreases with increasing amounts of calcium carbonate (CaCO<sub>3</sub>) in loamy textured soils. Maintaining B in the soil solution is important for plant nutrition (Keren & Bingham 1985; Keren *et al.* 1985) and it is controlled by the B in other soil fractions and their equilibrium with soil solution B.

Table 1. Estimate of boron (B) fractions in different calcareous soils (Soil I – 7.5, Soil II – 21.0 and Soil III – 47.5 calcium carbonate g/kg soil) of Punjab, India (mg B/kg soil)

Fractions	Soil I	Soil II	Soil III
Rs-B	0.34	0.34	0.31
Spa-B	0.35	0.40	0.65
Ox-B	0.15	0.15	0.16
Org-B	1.38	1.48	1.38
Res-B	54.7	64.3	89.1
T-B	56.9	66.7	91.6

Rs-B, readily soluble boron; Spa-B, specifically adsorbed B; Ox-B, oxide bound B; Org-B, organically bound B; Res-B, residual B; T-B, total B.

### Specifically adsorbed boron

The specifically adsorbed boron (Spa-B) fraction may be specifically adsorbed onto clay surfaces or associated with OM in soil (Jin *et al.* 1987), and depends mainly upon the clay content of the soil. It is the other fraction, after Rs-B, which is available for plant uptake (Jin *et al.* 1987, 1988; Tsalidas *et al.* 1994). This pool constitutes 0.01–0.61% of total soil B (Xu *et al.* 2001). Similar amounts of the fraction were reported by Padbhushan & Kumar (2015a) in the alkaline calcareous soils of Punjab (Table 1); these authors found that the amount increased slightly on soil B application. Boron adsorption occurs on the clay edges of illite (Couch & Grim 1968) and montmorillonite (Keren *et al.* 1981). Illite has a greater proportion of edge surface area than montmorillonite.

### Oxide-bound boron

The oxide bound boron (Ox-B) fraction is associated with oxides and hydroxides of Fe and Al. Manganese (Mn) forms a part of the structure through isomorphous substitution (McLaren & Crawford 1973; Tessier *et al.* 1979; Shuman 1985). It is a less labile fraction of B, which sorbs B into unavailable forms (Jin *et al.* 1988). Boron sorption behaviour in soils has indicated that Al and Fe oxide minerals play an important role (Harada & Tamai 1968; Bingham *et al.* 1971; Elrashidi & O'Connor 1982). This pool constitutes <3% of total boron (T-B) (Hou *et al.* 1994).

### Organically bound boron

Hou *et al.* (1994, 1996) included OM-bound forms in their proposed B fractionation procedure. The

organically bound fraction is bound to several forms of OM (detritus, organic coatings on mineral particles and humus bound fraction). Organic matter adsorbs B (Goldberg 1997), which is then unavailable for plant uptake (Hou *et al.* 1994). This fraction constitutes 2–8% of T-B.

#### Residual boron

The largest proportion among all fractions of B is composed of residual boron (Res-B) and it does not relate with plant available B (Jin *et al.* 1987; Tsalidas *et al.* 1994; Padbhushan & Kumar 2015b). Residual B is associated with primary and secondary minerals within the crystal structure and constitutes a substantial portion of T-B that is unlikely to be released in the mid- and long-term under the conditions normally found in native soils (McLaren & Crawford 1973; Tessier *et al.* 1979; Shuman 1985; Chao & Sanzalone 1989). The residual fraction is a non-labile form of B. This pool constitutes about 87.4–99.7% of T-B.

#### Total boron

The T-B concentration in soil varies according to its parent material and degree of weathering (Barber 1995): the range of T-B in agricultural soils is 2–100 mg/kg (Swaine 1955). In most Indian soils, the content has been found to vary between 3.8 and 630 mg/kg (Takkar 1982). Hadwani *et al.* (1989) observed that the total B content decreased with soil depth in all profiles. The T-B content of a soil is not a reliable indicator of available B for plant uptake (Nable *et al.* 1997).

#### RELATIVE PROPORTION OF BORON FRACTIONS

The relative proportion of various B fractions in soils depends upon various factors, especially inherent properties as well as soil application of B fertilizers. The parent material, texture, OM content, clay content and the microbial activities determine the extent of particular B fractions in the soil. Residual B constitutes the major proportion of T-B, which is not available for plant uptake. Hou *et al.* (1994) reported that Res-B accounts for about 99% of T-B in soils of Ontario. Xu *et al.* (2001) observed that non-specifically adsorbed boron (Nsa-B), Spa-B and Ox-B comprised 0.06–0.99, 0.01–0.61 and 0.03–7.57% of T-B, respectively. Raza *et al.* (2002) studied nine composite

surface soil samples collected from south-western and north-eastern agricultural regions of Saskatchewan and found that the mean contents of extractable B were 1.02% of the total B in Rs-B, 0.69% in Spa-B, 0.40% in Ox-B and 0.86% in organically bound boron (Org-B). About 92–97% of T-B was in Res-B or occluded fraction. Datta *et al.* (2002) collected 17 surface soil samples from different locations of India and reported that T-B ranged from 31 to 355 mg/kg. The Rs-B, Spa-B, Ox-B and Org-B constituted 0.38, 0.34, 1.45 and 0.62% of T-B, respectively. Residual B accounted for the major portion of T-B with a mean of 97.1%. Padbhushan & Kumar (2015b) reported that T-B in soil samples collected from Punjab, India, with CaCO<sub>3</sub> contents of 7.5, 21.0 and 45.6 g/kg soil, were 56.9, 66.7 and 91.6 mg/kg, respectively. The Rs-B in these soils varied from 0.60, 0.50 and 0.34% of T-B for these. It accounted for <1% of T-B. Specifically adsorbed B was 0.61, 0.60 and 0.71%, Ox-B was 0.26, 0.23 and 0.16%, Org-B was 2.42, 2.22 and 1.51% and Res-B was 96.1, 96.4 and 97.3% of the T-B for the three soils, respectively. Overall, the contents of B followed the order of Res B > Org-B > Spa-B > Rs-B > Ox-B. The extent of all fractions may vary depending upon the extent of influencing factors in the soils.

#### FACTORS INFLUENCING BORON FRACTIONS IN SOIL

##### Climate

Climate is the predominant factor affecting soil properties and B fractions. Increased rainfall and temperature increases the adsorption of B as the Fe–Al oxides and oxyhydroxides and the Mn-oxyhydroxides that will contribute to declining extractable B levels. This is due to the ligand exchange phenomenon, as suggested by Bingham *et al.* (1971). Xu *et al.* (2001) explained that decline in B content is correlated with increasing rainfall; this may be attributed in part to prolonged leaching losses of B in soils that receive high precipitation. However, the content of mineral fractions in the soils that adsorb B, such as the amorphous Fe–Al oxides and oxyhydroxides and the Mn-oxyhydroxides, also increase with increasing precipitation, and this will also contribute to declining extractable B levels. The distribution of B in various fractions was also related to site rainfall and temperature. The content of Nsa-B fraction significantly decreased with increasing mean annual rainfall (Xu

*et al.* 2001). This is due to stronger B leaching regime in the regions with more abundant rainfall. No clear relationship has been documented between Spa-B fraction and climate. A negative correlation has been recorded between Ox-B and rainfall and temperature (Xu *et al.* 2001). No significant correlation has been observed between Res-B and climate factors.

### Soil pH

Soil pH is one of the important factors, which influence the extent of many fractions of B in soils. The content of water-soluble B in soils tends to increase with soil pH, but not always in a consistent manner (Tsalidas *et al.* 1994), because B adsorption by soil components also increases with the increase in soil pH and reaches a maximum in the alkaline pH range (Gu & Lowe 1990; Goldberg *et al.* 1993, 1996). The content of Nsa-B fraction has been shown to increase significantly with increasing pH. Tsalidas *et al.* (1994) found that the Spa-B fraction was correlated with soil pH. No significant correlation was observed between Ox-B, Org-B, Res-B and soil pH. Hou *et al.* (1994) carried out sequential fractionation of B in mineral and synthetic soils and recorded that Rs-B was positively correlated with pH. Goldberg (1997) reported that adsorption of B exhibited a peak around pH 8–9. Xu *et al.* (2001) observed that Nsa-B increases significantly with increasing pH. No significant relations with other fractions of B were observed. Datta *et al.* (2002) reported in Indian soils that the Rs-B fraction has a positive relationship with pH (Table 2). The positive effect of soil pH on Rs-B is ascribed to the fact that increasing pH increases the negative surface charges of clays and other variable surface charges (Hingston 1964). Datta *et al.* (2002) also reported that the amount of Rs-B was approximately the same up to pH 7.0, and beyond this pH range a spectacular increase occurred (Table 2). Datta *et al.* (2002) did not find any relation between pH and other B fractions. The occurrence of Rs-B in the soils is correlated with soil pH, while other fractions are not.

### Soil organic matter

Organic matter plays an important role in adsorption and desorption of B: soil organic matter (SOM) adsorbs more B than mineral soil constituents (Yermiyaho *et al.* 1988; Gu & Lowe 1990). A possible mechanism for B sorption by OM is ligand exchange (Yermiyaho *et al.* 1988). However, Jin *et al.* (1987)

found no significant correlation between Spa-B and SOM. Hou *et al.* (1996) reported that OM plays an important role in determination of fractions of B and proposed a method for extraction of Org-B; although the scientific community was slow to recognize this, it was later accepted that OM does influence Org-B. A significant correlation was observed between Org-B and OM while no significant correlation was observed between Rs-B, Spa-B, Ox-B, Res-B and OM (Datta *et al.* 2002) (Table 2). A significant positive correlation between Org-B and OM was observed in different calcareous soils of India, Punjab (Padbhushan & Kumar 2015a). This may be because Org-B binds with OM and any increase in the content in OM increases the Org-B in soils.

### Clay content

Clay plays a major role in B sorption, both in terms of quantity of clay and the type of clay. The magnitude of B sorption in soil is greater in soils with greater clay fractions and *vice versa* (Xu *et al.* 2001). As the clay content increases in the soil, the sorption of B also increases. Boron availability depends upon the nature of clay present in the soil. Illite has greater clay edge surface area compared with montmorillonite (Couch & Grim 1968; Keren *et al.* 1981). Thus, B sorption is greater in illitic soil, as observed in the soils of Indian Punjab (Padbhushan & Kumar 2015a). Jin *et al.* (1987) reported a positive correlation between Spa-B and clay content, while Tsalidas *et al.* (1994) found that Spa-B was not correlated with clay content. Similarly, Xu *et al.* (2001) was not able to observe any relationship between B fractions and clay content in Chinese soils. Although a significant correlation is expected between the clay content of the soils and the Spa-B, the literature must be critically examined where the correlation is not observed. This could happen when the soils involved in the correlation study are similar in terms of clay content, or when illite is not the dominant clay mineral, or even when the content of illite is similar among the soils studied. Although Hou *et al.* (1996) reported that in addition to Spa-B, Res-B content was also correlated significantly with clay content.

In general, Spa-B and Org-B are positively correlated with clay content in soil. Residual B was also found to be significantly and positively correlated with clay content, as Res-B is the structural constituent of clay. A similar correlation for Res-B and clay was reported by Datta *et al.* (2002). No significant

Table 2. Simple correlation coefficients (*r*) between boron fractions and physicochemical properties of different soils of India

Boron fraction	pH	OC	Properties			
			Clay	Al*	Fe*	Al+Fe*
Rs-B	0.60 ( <i>P</i> < 0.01)	-0.06	0.23	0.20	-0.30	0.07
Spa-B	0.13	0.35	0.19	0.22	0.26	0.27
Ox-B	0.02	0.06	0.36	0.41	0.56 ( <i>P</i> < 0.05)	0.54 ( <i>P</i> < 0.05)
Org-B	-0.26	0.82 ( <i>P</i> < 0.01)	0.51 ( <i>P</i> < 0.01)	0.56 ( <i>P</i> < 0.05)	0.54 ( <i>P</i> < 0.05)	0.60 ( <i>P</i> < 0.01)
Res-B	-0.12	0.24	0.58 ( <i>P</i> < 0.05)	0.60 ( <i>P</i> < 0.05)	0.66 ( <i>P</i> < 0.01)	0.69 ( <i>P</i> < 0.01)

OC, organic carbon; Al, aluminium; Fe, iron; Rs-B, readily soluble boron; Spa-B, specifically adsorbed boron; Ox-B, oxide-bound boron; Org-B, organically bound boron; Res-B, residual B.

\* NH<sub>4</sub>-oxalate extractable (pH 3.25).

correlation was observed between Rs-B and Ox-B (Table 2). Padbhusan & Kumar (2015a) observed a significant positive correlation between Ox-B, Res-B and clay content. This was due to an increase in clay content, which increases the surface area of the soil resulting in more Ox-B in the soil; also because Res-B is the structural constituent of clay, which ultimately results in an increase in the amount of Res-B with an increase in the clay content of soil.

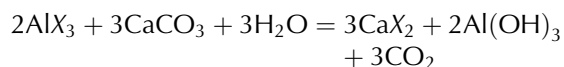
#### Ammonium-oxalate extractable iron and aluminium

Hou *et al.* (1994) and Datta *et al.* 2002 failed to establish a positive relationship between the Spa-B and ammonium (NH<sub>4</sub>)-oxalate extractable Fe and Al. This fraction probably originates from the weak binding site of both organic and inorganic constituents. However, it was later observed that the NH<sub>4</sub>-oxalate extractable Fe and Al increased with increasing precipitation and contributed to declining extractable B levels (Xu *et al.* 2001). A significant correlation was observed between Ox-B, Org-B, Res-B and NH<sub>4</sub>-oxalate extractable Fe and Al. This is due to the acidic dissolution and/or complexation mechanism, while no significant correlation was observed with Rs-B and Spa-B (Datta *et al.* 2002) (Table 2).

#### Calcium carbonate

No significant correlation has been found between CaCO<sub>3</sub> and water-soluble fraction of soils (Bhattacharjee 1956; Gandhi & Mehta 1958; Mathur *et al.* 1964; Grewal *et al.* 1969; Singh & Randhawa 1977). However, Paliwal & Mehta (1973) found that in the soils of Kota and Bhilwara regions of Rajasthan, water-soluble B was negatively related to

CaCO<sub>3</sub> content (*r* = -0.63, *P* < 0.01), and Elseewi & Elmalky (1979) found that the acid-soluble fraction of B was negatively related with CaCO<sub>3</sub> content of the soil. Sims & Bingham (1968) threw considerable light on the nature of B retention and provided a better understanding of the reactions involved in B fixation. As the main reaction occurs when acid soils are limed, the replacement (by calcium) of exchangeable Al, and hydroxyl-Al cations, occurs with their resulting precipitation as aluminium hydroxide (Al(OH)<sub>3</sub>). The adsorption of B on Al(OH)<sub>3</sub> was studied by Hatcher *et al.* (1967), who demonstrated that freshly precipitated Al(OH)<sub>3</sub> adsorbed large quantities of B, while adsorption decreased markedly with time. The reaction between exchangeable Al and lime may be summarized as follows:



where X is the exchange site. The freshly precipitated Al(OH)<sub>3</sub> is then available for adsorption of B. The CaCO<sub>3</sub> content of salt-affected soils in Punjab was found to be significantly correlated with the available and T-B (Sharma 1984).

#### RELATIONSHIP BETWEEN BORON FRACTIONS

To understand the dynamics, transformation and bio-availability of B, interactions between various B fractions are important. Interactions between various B fractions determine the status of the fractions resulting from uptake of B at later stages of crop growth. The readily soluble fraction quantity is reduced in the later stages of crop growth, leading to a belief that it might be converted into other fractions of B. Tsalidas

*et al.* (1994) carried out work in Greek soils and reported no correlation between any of the B fractions. Hou *et al.* (1996) investigated interaction between B fractions and observed that Nsa-B had a close correlation with oxide- and hydroxide-bound B. Xu *et al.* (2001) observed the interaction between the various B fractions in Chinese soils and concluded that Nsa-B was positively correlated with oxide B forms such as Moh-B and B occluded in crystalline Fe and Al oxides (Cro-B) fractions. There was also a close relationship between Spa-B and Moh-B (Table 3), and Spa-B was negatively and significantly correlated with Rs-B (Padbhushan & Kumar 2015a). This showed that as the time passed, the readily soluble fraction transformed into Spa-B, while no significant relation was observed with other B fractions. To date, very few investigations have been carried out into the relationships between B fractions. More studies are needed to determine the dynamics, transformation and bioavailability of B. Similarly, more studies on interactions between the different fractions of B in different soils with B fertilization are needed.

#### RELATIONSHIP OF EXTRACTABLE BORON WITH BORON FRACTIONS

Jin *et al.* (1987) compared the B fractions with various extractants in 14 temperate soils and presented different proportions of B: they reported that calcium chloride ( $\text{CaCl}_2$ ) as an extractant has a high proportion of Nsa-B. Similar results were reported by Badr-Uz-Zaman & Salim (1999), who studied eight soils in Pakistan and reported that little B extracted by  $\text{CaCl}_2$  was in non-specifically adsorbed form. The proportion of Nsa-B ranged from 0.4 to 2.3% with an average value of 1.2%. The Spa-B, from the soil extracted with mannitol, was 14.2–19.2% of total soil B with a mean content of 17.4%. Raza *et al.* (2002) reported that an average of 1% of the total soil B was present as hot water-soluble B. The 0.01 M  $\text{CaCl}_2$  and 1 M  $\text{NH}_4$ -acetate extracted 0.74 and 0.37% of the total soil B, respectively. The major portion of soil B existed in the residual or occluded form. This was also reported when 0.01 M  $\text{CaCl}_2$ , 1 M  $\text{NH}_4$  acetate and anion exchange membranes were used as Rs-B extractants.

Datta *et al.* (2002) observed that hot  $\text{CaCl}_2$  extracted the highest amount of B followed by salicylic acid, hydrochloric acid, tartaric acid,  $\text{NH}_4$  acetate ( $\text{NH}_4\text{OAc}$ ) at pH 4.8,  $\text{CaCl}_2$  + mannitol and  $\text{NH}_4\text{OAc}$  (pH 7.0). Stepwise regression indicates that

75% of the variability in hot  $\text{CaCl}_2$  extractable B (Hcc-B) could be attributed to Rs-B, Spa-B, Ox-B and Org-B. The Spa-B and Org-B fractions could explain 80% of the variability in salicylic acid extractable B (Sa-B), whereas Rs-B and Spa-B fractions could account for 64% of the variability in  $\text{CaCl}_2$  + mannitol extractable-B (Caml-B). Specifically adsorbed B accounted for 56% of the variation for  $\text{NH}_4\text{OAc}$  (pH 4.8) extractable-B, while Rs-B and Res-B could explain 48% of the variation in HCl extractable-B (HCl-B). Residual B, Spa-B and Org-B could explain 65% of the variation in tartaric acid extractable-B (Ta-B). Since Hcc-B and Sa-B extractants isolate the highest amount of B from the soil samples, they are more capable of extracting Rs-B, Spa-B and Org-B fractions and are also better predictors of plant available B in soils (Table 3). The extractable B was found to be positively related with organic carbon (Mandal *et al.* 2016).

#### FRACTIONATION TECHNIQUE FOR SOIL BORON

Various fractionation techniques have been developed for soil B using methods originally developed for selective dissolution of trace metals, in which a particular fraction of the element might be removed by a specific extractant. Jin *et al.* (1987) developed a separate extraction scheme to determine the distribution of B between different fractions in soils. Hou *et al.* (1994, 1996) modified this scheme and developed a sequential fractionation method for partitioning total soil B among different distinct pools. Datta *et al.* (2002) proposed colorimetric method to determine the various forms of B and later Padbhushan & Kumar (2015a) developed the procedure using combined colorimetric (Rs-B and Spa-B) and ICAP-AES (inductively coupled plasma atomic emission spectroscopy) (Ox-B, Org-B and Res-B) to estimate the different B forms. A flow diagram for fractionation of B in soils as proposed by Datta *et al.* (2002) and Padbhushan & Kumar (2015a) is presented in Fig. 1.

Another sequential extraction scheme for B in soils and sediments is shown in Hou *et al.* (1996) for synthetic and mineral soil.

#### PLANT RESPONSE

Hot water-extractable B has been regarded as a suitable index of plant-available B (Bingham 1982), but in some studies, levels of hot water-extractable B

Table 3. Correlation coefficients (*r*) between various soil boron (B) fractions for Chinese soil

Boron fractions	Hws-B	Nsa-B	Spa-B	Moh-B	Amo-B	Cro-B	Res-B
Hws-B	1.00						
Nsa-B	0.31	1.00					
Spa-B	0.20	0.21	1.00				
Moh-B	0.34	0.62 ( $P < 0.05$ )	0.72 ( $P < 0.01$ )	1.00			
Amo-B	0.00	-0.34	-0.30	-0.43	1.00		
Cro-B	0.32	0.68 ( $P < 0.05$ )	-0.09	0.40	-0.29	1.00	
Res-B	-0.07	-0.02	-0.34	-0.30	0.11	0.10	1.00

Hws-B, Hot water-soluble B; Nsa-B, non-specifically adsorbed B; Spa-B, specifically adsorbed B; Moh-B, B occluded in Mn-oxyhydroxides; Amo-B, B occluded in amorphous Fe and Al oxides; Cro-B, B occluded in crystalline Fe and Al oxides; Res-B, residual B.

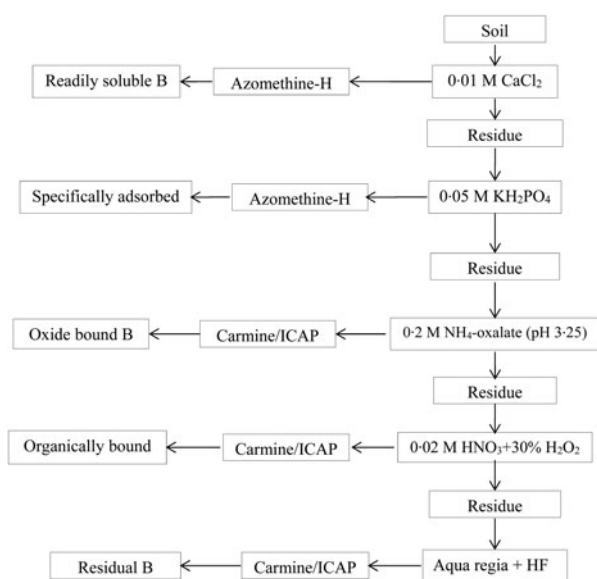


Fig. 1. Flow diagram for the fractionation of boron in soils.

have not been correlated with plant response (Sims & Johnson 1991), suggesting that a better understanding is needed of the pools of soil B accessed by prevailing soil B tests and their relationship to plant B uptake (Bell 1997). Moreover, the available forms of soil B vary with plant species (Tsalidas *et al.* 1994). Jin *et al.* (1987) found that B concentration in maize tissue correlated positively not only with Ws-B, but also with Nsa-B, Spa-B and Mho-B. Tsalidas *et al.* (1994) showed that B content in olive tree (*Olea europaea* L.) leaves correlated well with amorphous Fe–Al oxyhydroxide-occluded B, Spa-B and Mho-B besides WS-B. By contrast, in barley (*Hordeum vulgare* L.) leaves B content was correlated with Nsa-B as well as amorphous Fe–Al oxyhydroxide-occluded B, Spa-B and WS-B, but not with Mn-oxyhydroxide-occluded

B (Tsalidas *et al.* 1994). It remains to be demonstrated that the Mn-reducible and Org-B fractions can be clearly distinguished and such a distinction is important for predicting plant response to soil B.

Jin *et al.* (1988) concluded that oxyhydroxides of Al and Fe sorb B into unavailable forms. Thus, the Nsa-B, Spa-B and Moh-B fractions may be most readily available to plants (Jin *et al.* 1987, 1988; Tsalidas *et al.* 1994), although this needs further investigation. In 13 Chinese soils examined, 87.4–99.7% of soil B was in the residual fraction (Res-B), which generally does not relate well to plant-available B (Jin *et al.* 1987; Tsalidas *et al.* 1994). Therefore, a better understanding of the distribution of B in various soil fractions and their relationships with plant response would provide a basis for assessing the availability of soil B to plants and formulating field management practices to influence B availability. This need is especially evident in areas where soils contain low levels of B and deficiency is a significant limit to crop production (Shorrocks 1997).

For a green gram crop sown in B-deficient calcareous soils of Punjab (Padbushan & Kumar 2015b), at grand growth stage, a significant increase in Rs-B with B applications was recorded while at maturity there was a significant increase only up to a certain level of B application (0.75 mg B/kg). Readily soluble fractions decreased at maturity in comparison with the grand growth stage at different levels of soil applied B. This might be due to increased B uptake and transformation of readily soluble fraction to oxide bound and organically bound fraction at maturity. In the case of Spa-B at grand growth stage, there was no significant increase at any level of B application as compared with the control, while at maturity there was a significant increase only up to 0.75 mg

B/kg. In Ox-B at both stages of crop growth, there was a significant increase at all levels of B application. In Org-B at both stages of crop growth, there was no significant increase at any levels of B application as compared with the control. However, an increase in organically bound at maturity from grand growth stage was observed, numerically. This might be due to more OM addition in the soil. Total B decreased at maturity as compared with grand growth stage in green gram crop, which may be due to increase in B uptake by green gram crop from grand growth to maturity stage (Padbhushan & Kumar 2015b).

Boron application and soil type have a significant interactive effect on shoot dry weight. Widespread responses to B application on alkaline calcareous soils may be due to an increased B requirement by agricultural crops due to a widened Ca/B ratio in the soil–plant system (Fleming 1980; Tisdale *et al.* 1985).

## FUTURE STUDIES

In order to better understand the dynamics, transformation and bioavailability of B fractions, further studies on interactions between the different fractions in various soils with application of B fertilizers should be carried out. Relationships between various B fractions and their interactions with crop growth need to be understood for various soils.

## CONCLUSION

Boron fractionation of soils provides insights for qualitative and quantitative significance of B fractions. In general, Res-B forms the major fraction of T-B followed by Org-B, Spa-B, Rs-B and Ox-B, respectively. Residual B is significantly correlated with pH, climatic factors and CaCO<sub>3</sub> content in soils, Spa-B is significantly correlated with clay content of the soil, Ox-B is significantly correlated with climatic factor, NH<sub>4</sub><sup>+</sup>-oxalate extractable Fe and Al and Org-B is significantly correlated with OM content in soil. Among all fractions, Rs-B is the most available form for plant uptake. Transformation of Rs-B to different fractions of B takes place at maturity of crop. Nsa-B, Spa-B and Moh-B are found responsive to B uptake in plant.

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