BORON 2 (3), 111 - 122, 2017

BOR DERGİSİ

JOURNAL OF BORON

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Boron fertilizers: use, challenges and the benefit of slow-release sources – a review

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ARTICLE INFO

Article history:
Received 22 March 2017
Received in revised form 28 July 2017
Accepted 19 October 2017
Available online 30 December 2017

Review Article

Keywords:
Boron,
Toxicity,
Deficiency,
Leaching,
Slow-release fertilizer

ABSTRACT

Boron (B) is an essential plant nutrient, but can be toxic when present in excess. Boron is usually present as an uncharged molecule ($H_3BO_3^0$) in the soil solution and is highly mobile in most soils. Deficiency of B is therefore quite common in high-rainfall environments, especially on sandy soils. Boron fertilizers are commonly used to correct its deficiency in crops. The most commonly used fertilizers are soluble sodium borates (e.g., borax), but care should be taken with rates and placement of such B products, since elevated B concentrations may result in seedling toxicity and yield reduction. Moreover, significant leaching losses of applied B may occur in high-rainfall environments. Slow-release B sources reduce both the risk of seedling toxicity and of leaching, and can provide adequate supply of B over a longer period. This may allow for lower B rates or less frequent application compared to soluble fertilizers. The most commonly used slow-release B sources are sparingly soluble ores, such as colemanite. The limited data in the literature indicate that the release rate of B from slow-release sources in soil depends both on fertilizer characteristics and soil properties. However, more research is needed to predict the release rate of B from various B ores for given soil and climatic conditions. In recent years, slow-release coatings and matrices for N fertilizers have received considerable attention and these new technologies may potentially also be adopted for B-containing fertilizers.

1. Introduction

Boron (B) is an essential micronutrient, required for normal growth and development of plants [1]. Under normal soil conditions, B in soil solution is present as boric acid (H_3BO_3), a non-ionized molecule. The retention of H_3BO_3 in soils is weak, making it vulnerable to leaching. Hence, B deficiency is most commonly observed in coarse-textured soils in high rainfall regions [2]. Boron toxicity occurs most commonly in arid or semi-arid regions because of high natural B levels or because of the addition of B with irrigation water [3].

Boron fertilizers are used to correct B deficiency, but B fertilization can be challenging because of the narrow window between deficiency and toxicity and the limited mobility of B within most plants. High B concentrations at seedling stage may result in seedling toxicity, while leaching losses may result in insufficient B later in the season. Boron is notoriously known as the element for which toxicity and deficiency may occur concurrently in the same plant [4]. This review discusses B fertilization, with particular focus on the use of slow-release fertilizers to overcome the aforementioned challenges.

2. Boron chemistry and mobility in soil

Boron is a member of the metalloid group and has intermediate properties between metals and non-metals. Essentially all B is in a trivalent (+3) oxidation state, but unlike its neighbour Al, B does not exist as trivalent cation but generally forms covalent bonds [5]. Boron in soil solution is present mainly as boric acid (H_3BO_3) or at high pH also as borate ($B(OH)_4^-$), since the pK_a is 9.24. Boron adsorption by soil components is generally weak, and may occur on phyllosilicate clays [6], oxides and hydroxides [7], carbonate minerals [8] and organic matter [9].

Boron adsorption is dependent on soil properties. The adsorption increases with increasing pH, reaching a maximum around pH 9 [10]. Keren et al. [11] developed a phenomenological adsorption equation that takes into account the effect of pH on B adsorption, which was also applied to describe B adsorption by whole soils [12]. The equation can be written in the

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$$s = s_{\max} \cdot \frac{Kc}{1+Kc} \qquad (1)$$

with s the adsorbed B concentration (mol kg^{-1}), c the B concentration in solution (mol L^{-1}) and K a pH-dependent adsorption coefficient (L mol^{-1}):

$$K = \frac{K_{\mathrm{BH}} + 10^{\mathrm{pH}} K_{\mathrm{a}}.K_{\mathrm{B}}}{(1+10^{\mathrm{pH}} K_{\mathrm{a}})(1+K_{\mathrm{OH}}.10^{(\mathrm{pH}-14)})} \qquad (2)$$

The constants K_{BH}, K_{B} and K_{OH} represent empirically defined affinity coefficients for binding of H_3BO_3 or $B(OH)_4^-$ and OH^- to B-specific adsorption sites and K_a is the hydrolysis constant of H_3BO_3 (value of 5.9×10^{-10} at 25 °C). The adsorption maximum, $s_{\max}$, is soil dependent and has been found in several studies to correlate most closely with clay content and/or CEC. Following relationship was derived from literature data [12-14]:

$$s_{\max}\ (\mathrm{mol\ kg^{-1}}) = \mathrm{clay}\ (\%) \times 0.14 + 0.34 \qquad (3)$$

Based on this relationship and typical affinity coefficients reported in the literature [12], estimated Langmuir parameters for soils with different pH and clay content were derived (Table 1; parameters converted from mol- to mg-basis for easier comparison with most published values). The corresponding sorption isotherms are illustrated in Figure 1. A decrease in soil pH below 7 is expected to have little effect on B sorption, whereas an increase in soil pH from pH 7 to 9 strongly increases sorption. These values are only estimates, as other soil properties (e.g., organic matter, type of clay minerals, etc.) may also affect B sorption, but these sorption isotherms are useful to discuss the effect of soil properties on mobility of B. The Langmuir isotherm can be simplified to a linear relationship in the low concentration range ($c < K^{-1}$).

$$s \approx s_{\max} \cdot K \cdot c = K_{\mathrm{d}}.c \qquad (4)$$

Other sorption models have also been applied to model the adsorption behavior of B in soils. The empirical Freundlich model generally describes the sorption isotherms well, but only applies for the soil and the conditions evaluated. Surface complexation models describe adsorption using an equilibrium approach, accounting for surface and aqueous speciation changes as a function of pH and solution composition. The most commonly used surface complexation model to describe B sorption in soils is the constant capacitance model, which has been found to successfully describe B sorption over a range of soils [15].

Overall, the literature results indicate that B adsorption is weak in most soils. The strongest sorption is seen in soils with high clay content and high pH (8 or higher), but in soils with pH 7 or less, the retention is weak even in soils with heavy texture. Given the weak adsorption and hence high mobility of added B in most soils, one would expect soils in high rainfall environments to be mostly depleted in B. However, most soils have a total B concentration between 10 and 100 mg kg^{-1}, but only a small part is in readily available form. Most of this B is in a sparingly soluble form, as several minerals in soils contain B as a structural component. The B content of phyllosilicates in particular is higher than that of most other minerals [16], explaining why often a positive correlation is seen between clay content and B concentration of soils. For instance, in a dataset with 17 European soils [17], there was strong correlation (r=0.89) between clay content and total soil B concentration. In general, soils rich in clay have higher B concentration than sandy soils [18]. Boron occluded in minerals may already have been present in the parent material, but may also originate from added B that has become irreversibly sorbed. Several studies have shown strong hysteresis in B sorption [19], which may be related to incorporation of B into tetrahedral sites of clay minerals [20].

As B retention is weak in most soils, B added in soluble form (boric acid or borate) can easily leach. Indeed, it has been long known that added fertilizer borate is vulnerable to leaching. For example, Kubota et al. [21] investigated leaching of borax in 10 field sites and observed that most B moved to a depth of 60 cm or

Table 1. Estimated Langmuir parameters ($s_{\max}$ and K) for B sorption in soil depending on soil pH and clay content. The K_d is the corresponding solid:liquid distribution coefficient at low B concentrations ($c<K^{-1}$).

pH	clay (%)	$s_{\max}$ (mg kg^{-1})	K (l mg^{-1})	K_d (L kg^{-1})
7	5	11	0.021	0.2
8	5	11	0.039	0.4
9	5	11	0.092	1.0
7	20	34	0.021	0.7
8	20	34	0.039	1.3
9	20	34	0.092	3.1
7	50	79	0.021	1.7
8	50	79	0.039	3.1
9	50	79	0.092	7.3

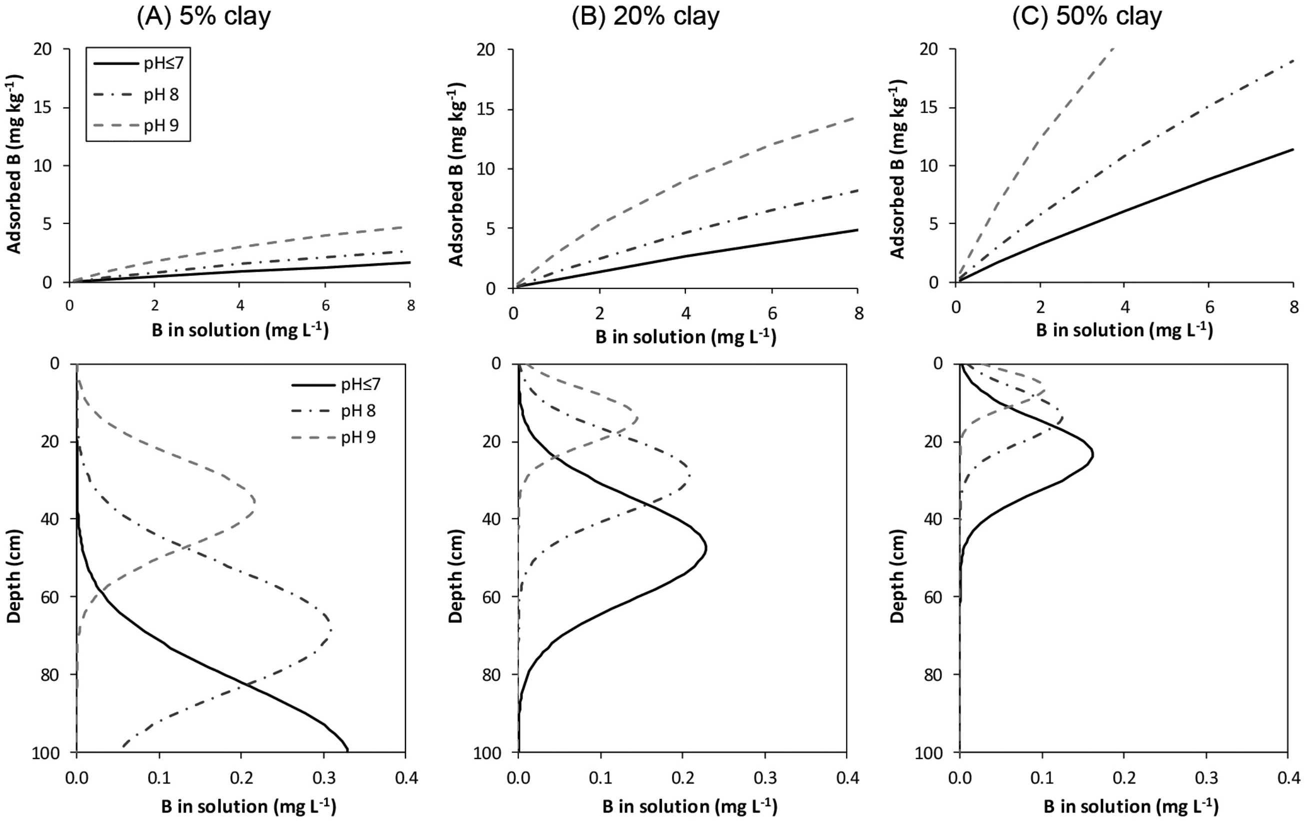

Figure 1. Estimated sorption isotherms (top) and corresponding leaching profiles for 1 kg ha^{-1} soluble B applied at the surface after 60 cm of rainfall (bottom) for a soil with clay content of 5% (A), 20% (B), or 50% (C) and pH values as indicated in the graphs. The leaching profiles were modelled with Hydrus-1D [69], assuming a bulk density of 1.5 kg L^{-1}, volumetric water content of 0.25, water flux (Darcy) of 0.3 cm d^{-1} and dispersion length of 2 cm.

deeper within 6 months in light-textured soils. Similarly, Winsor [22] reported that over 85% of added borax was leached below 1 m depth after 40 cm rainfall over a 4-months period. Laboratory studies have confirmed the rapid movement of applied B in most soils [21, 23]. For instance, in a loamy sand soil at pH 6.9, breakthrough of B was observed after about 3 pore volumes [23]. Given that K_d values for B sorption are <1 L kg^{-1} in most soils except those with high pH and heavy texture (Table 1), a retardation coefficient (R) of <5 is expected for most soils, i.e., B is expected to move <5 times slower compared to the water movement, which is much quicker than most other trace elements, which generally have K_d values >10 L kg^{-1} (i.e. R>50). The high mobility of B is also illustrated in Figure 1, which shows the movement of B added onto the soil surface at a rate of 1.0 kg B ha^{-1} after 60 cm of rainfall using the Langmuir sorption parameters estimated for the various soil scenarios (Table 1).

3. Boron in plants: deficiency and toxicity

Plants take up B from the soil solution. It was long believed that the uptake occurred only *via* a passive diffusion process through the lipid bilayer [24]. However, research in recent decades has demonstrated the presence of channel-mediated facilitated diffusion and energy-dependent active transport, involving membrane transporters whose activity is regulated in response to B conditions [25].

The fact that B is essential for plants has been recognized since the 1920s [26], but it is only in recent decades that the molecular basis of this requirement has been unravelled. An important function of B in plants is the dimerization through borate cross-linking of a pectic polysaccharide (rhamnogalacturonan II, RG II) that is essential for cell wall integrity [25]. Apart from cross-linking of pectins, B has also been suggested to be essential for membrane function and metabolic activities [27].

In most plant species, B has restricted mobility, which means it cannot be easily remobilized from older to new plant parts. However, in plant species that produce significant amounts of polyols (sorbitol, mannitol) in source leaves, such as the woody Rosacea (apple, pear, *Prunus* spp.), B has been found to be phloem-mobile, which is attributed to the formation of B-polyolcomplexes [28]. Boron deficiency in crops occurs if the B supply is insufficient to maintain B concentration in the plant at the level required for optimal growth. Because B is essential for cell wall development of the generative organs and is not phloem-mobile in most species, adequate supply is critical during the reproductive phase [29]. Due to the limited mobility, deficiency symptoms typically occur in meristematic tissue (i.e., buds and young leaves) [28] (Figure 2). Plant species sensitive to B deficiency are mostly plants with relatively high B requirement and include *Cruciferae*

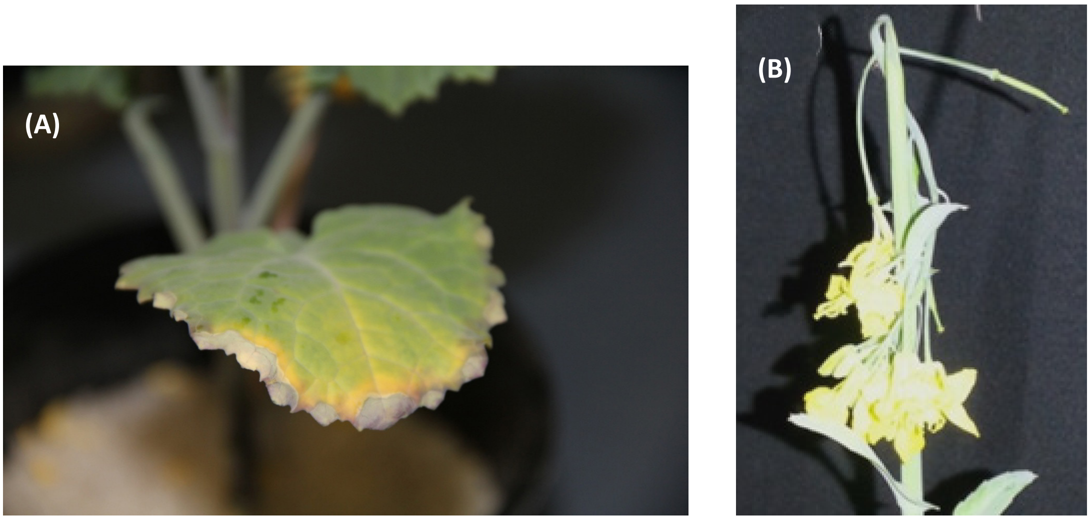

Figure 2.(A) Toxicity symptoms observed in a first crop of canola grown on soil treated with MAP cogranulated with borax (1% B); and (B) deficiency symptoms observed in a second crop of canola grown on the same soil that was submitted to leaching. Pictures from ref. [67].

(e.g., cabbage, cauliflower), some of the *Chenopodiacea* (e.g., sugar beet) and several fruit trees (e.g., apple, pear) [2].

While inadequate supply of B impairs plant growth, excess B can also have negative impact. Visual symptoms of B toxicity depend on the mobility within the plant. In most species, B is phloem-immobile, and B toxicity is usually manifested as marginal leaf burn in older leaves (Figure 2). In contrast, species in which B is phloem-mobile usually exhibit B toxicity as die-back in young shoots, profuse gumming in the leaf axil and brown lesions along stems and petioles [28]. Boron toxicity is relatively rare compared to boron deficiency and occurs mostly in (semi-)arid regions. Managing B toxicity can be achieved through amelioration of the soil or by using crops with high tolerance to B toxicity [30].

Boron nutrition can be challenging, because compared to most other nutrients, the range of optimal supply is relatively narrow, as is illustrated in Figure 3. The B uptake by plants is proportional to the concentration of available B in the medium. Growth reduction due to deficiency or toxicity can be related to internal tissue concentrations. If the supply is in the deficient range, B concentration in the tissue will fall to a minimum level required for optimal growth and plant growth will be reduced. Conversely, if the supply is in the toxic range, internal concentrations will reach a toxic level above which yield is also depressed. The threshold tissue concentrations for toxicity and deficiency depend on plant species and on the plant part, since B concentrations are usually not homogeneous within the plant but often higher in older than in new tissue. For the diagnosis of B deficiency, growing tissues need to be sampled if B is phloem-immobile, since the B concentration in matured leaves may not reflect the B status in the newly developing plant parts [28]. Critical B concentrations in the new leaves range from 2 to 20 mg kg^{-1} for most plant species, and tend to be lower for monocots than for dicots [31], likely because of the lower pectin content of monocots [29]. Internal thresh-

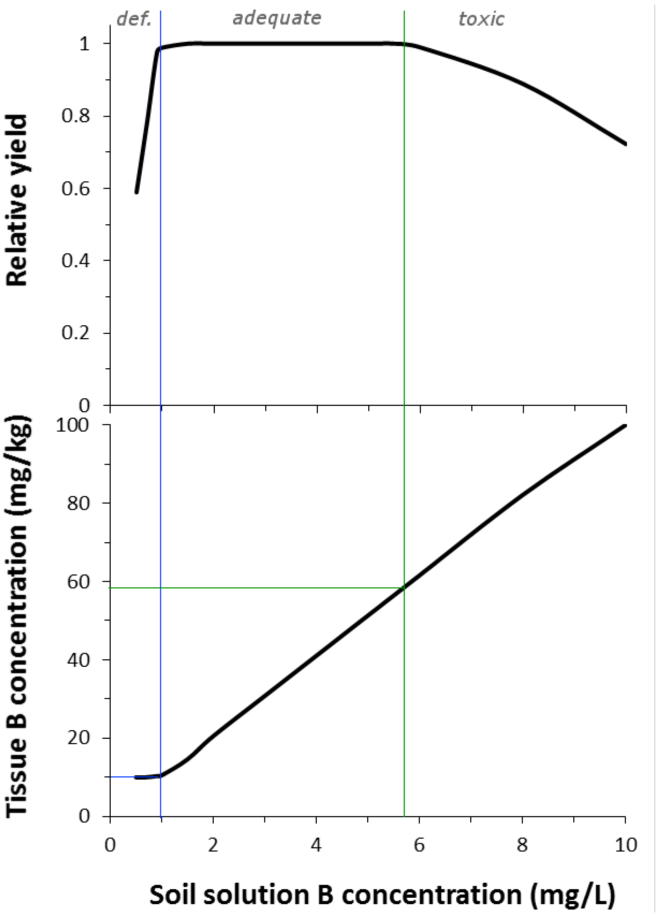

Figure 3. Hypothetical schematic illustration of the relationship between B supply (soil solution B concentration), B in plant tissue and relative yield. In this example, the deficient level (indicated by the blue lines) in the plant tissue is 10 mg kg^{-1} and the toxic level (indicated by the green lines) is 58 mg kg^{-1}, which corresponds to an adequate range of soil solution B concentration ranging from 1 to 5.5 mg L^{-1}.

old concentrations for toxicity are also plant genotype dependent but usually are in the order of 50-200 mg B kg^{-1} [31]. A higher tolerance to B toxicity of plant cultivars generally appears to be related to lower uptake (B exclusion), not to an ability to tolerate high tissue B concentrations [3]. However, some moderately tolerant species, e.g. *Gypsophila* sp., have been found to accumulate and tolerate relatively high tissue B concentrations [32]. In extremely B-tolerant species, such as *Puccinellia distans*, B tolerance seems to be the result of both B exclusion and high internal tolerance [32].

4. Soil testing

Given that large amounts of B in soil are occluded in minerals or irreversibly sorbed, it is no surprise that total B content is not a good predictor of plant availability. In general, B extractable with mild extracts, such as (hot) water, dilute (0.01 or 0.02 M) $CaCl_2$ or 0.01 M mannitol, show the best correlation with plant B concentrations [33]. Extraction with hot water is probably the most commonly used method to predict plant availability, and has performed well in many studies [34, 35]. However, in other studies, hot water extraction gave poor predictions [36] and the method has also been criticized because variation in heating and cooling rates, which changes the effective extraction time, is a significant source of variability [37]. In any case, results obtained with mild extractants such as hot water, cold water and dilute $CaCl_2$ generally correlate strongly with each other and therefore usually correlate similarly with plant uptake. Furthermore, no soil extract can ever give a perfect prediction of B availability to plants across soils and plant species, as plants may modify the rhizosphere soil and hence nutrient availability. For instance, Tsadilas et al. [38] tested a range of extractants and observed that B content in olive trees showed strongest correlation with ammonium-oxalate extractable B (i.e., oxide-associated) whereas B concentration in barley correlated most strongly with water-extractable B. Furthermore, extractions do not account for the water content under in situ conditions, but use a fixed liquid:solid ratio. Since B is only weakly buffered in soil, a lower water content results in a higher solution concentration. For instance, Mertens et al. [17] assessed the effect of B on root elongation of barley and found a positive relationship between ED50 (added B rate that causes a 50% reduction) and water content of the soil, which was attributed to more dilution of B at high water content. Also, hot water extraction and most other extracts also release adsorbed B that is not directly available to plants. Because of more adsorption in alkaline and heavy textured soils, plants generally take up more B in acid or light-textured soils at a given level of hot water-extractable B (HWB) [39]. Finally, soil extraction is usually carried out on the top soil, but the highest B concentrations often occur in the subsoil [30].

Despite these drawbacks, HWB extraction can give a useful indication of the B status of the soil, and is commonly used in guidelines regarding B status of the soil. HWB concentrations between 0.5 and 3 mg kg^{-1} are generally considered to be adequate, but this range also depends on crop species [37, 40]. For crops with low requirement, even 0.1 mg kg^{-1} may be sufficient [37].

5. Sources of boron

Boron is naturally present in soil, but concentrations vary widely, ranging from 1 to >200 mg B kg^{-1}, depending on the parent material and degree of weathering [41]. Boron is present in various minerals, e.g., in borosilicates and borates. Boron in minerals is often not readily soluble; usually, less than 5% of soil B is available for plant uptake [41]. Boron deficiency is most likely to occur in sandy soils in high-rainfall environments. Boron toxicity on the other hand is most likely to occur in (semi-) arid regions, where there is no or little removal by leaching and either the soil or irrigation water have high B level [42]. Irrigation water is one of the main sources of high soil B levels resulting in toxicity [36], because of its continued use and concentration in the soil due to evapotranspiration. Safe concentrations of B in irrigation water have been reported to be around 0.3 mg B L^{-1} for sensitive plants, around 1 mg B L^{-1} for semi-tolerant plants and 2-4 mg B L^{-1} for tolerant plants [43]. However, it should be kept in mind that the extent to which B will build up in the soil also depends on the excess irrigation water used, since a higher excess water results in more drainage and hence less build-up of B [44], so these values are only guidelines, and specific conditions need to be taken into account when assessing if irrigation water can safely be used without risking the accumulation of B in toxic amounts.

Boron fertilizers are sourced from borate mineral deposits. The borate deposits of commercial value were formed in continental basins by concentration of waters enriched with B from volcanic emission [45]. Colemanite, kernite, tincal (crude borax) and ulexite are the most common borate minerals. The annual world production of borate minerals is around 2.2 million tonnes, expressed as B_2O_3 equivalent, and agriculture is estimated to comprise 14% of its use [46]. Worldwide, borate minerals are mined in Turkey, the United States, South America (Andes), Russia and China. Approximately 70% of the world supply comes from two corporate organizations – Eti Mine Works (Turkey) and RioTinto (US Borax) [47]. It is estimated that 72% of the world's B reserves are located in Turkey.

6. Boron fertilization

6.1. Fertilizer sources

Boron fertilization is used in many B-deficient regions. The most common fertilizer sources are soluble sodium tetraborates (borax) in various states of hydration (Table 2). They are made by refining naturally occurring

Table 2. Boron compounds used as fertilizer

Compound (Common name)	Formula	% B
Borax and refined borates		
Disodium tetraborate decahydrate (borax penta)	$Na_2B_4O_7.10H_2O$	11.3
Disodium tetraborate pentahydrate (borax deca)	$Na_2B_4O_7.5H_2O$	15.2
Disodium octaborate tetrahydrate	$Na_2B_8O_{13}.4H_2O$	20.9
Anhydrous borax (dehybor)	$Na_2B_4O_7$	21.5
Boric acid	H_3BO_3	17.5
Crushed or refined ores[a]		
Kernite	$Na_2B_4O_6(OH)_2{\cdot}3H_2O$	14.9
Ulexite	$NaCaB_5O_9.8H_2O$	13.3
Colemanite	$Ca_2B_6O_{11}.5H_2O$	15.8
Hydroboracite	$CaMgB_6O_8(OH)_6{\cdot}3H_2O$	15.7
Datolite	$CaBSiO_4(OH)$	6.8
Howlite	$Ca_2B_5SiO_9(OH)_5$	13.8
Other sparingly soluble compounds		
Boron frits	(boric oxide glass)	2-11
Boron phosphate	BPO_4	10.2

[a] : The reported B contents are for the pure minerals. Fertilizer products may contain impurities and, hence, may have different B contents.

borax (tincal). The octaborate is made from borax and boric acid. It has high B content and is very soluble, making it the preferred source for foliar fertilizers. Boric acid is produced by reacting refined borax with sulphuric acid. It is highly soluble, but is not often used as fertilizer source because of its higher cost [45]. Several crushed ores have been used as potential slow-release sources and they are considered to be more suitable for use on sandy soils than borax [48]. Colemanite and ulexite are the ores most commonly used as B fertilizer sources. Other B ores mentioned in literature include kernite [49], datolite, hydroboracite [50], and howlite [51]. Furthermore, also B frits have been used as a slow-release B source. They are produced by melting silicates with powdered borates and their B concentration generally ranges between 2 and 11%. Another slow-release source is BPO_4, which is produced from phosphoric acid and boric acid [52, 53]. In recent years, also a few slow-release B fertilizers have been described in literature that use a slow-release matrix with borax incorporated [54, 55].

There are not many studies that compared various slow-release B fertilizers and because different studies often use different methods, comparison between studies is often not possible. Abat et al. [53] assessed the solubility and release rates of colemanite, ulexite, and of BPO_4 synthesized at different temperatures (Table 3). They found that ulexite was about 10 times more soluble than colemanite, in agreement with thermodynamic solubility calculations using published solubility products. The solubility of the BPO_4 compounds decreased with increasing synthesis temperature. Colemanite and ulexite had an alkaline reaction in water and their solubility increased by acidifying the solution to pH 5, whereas the BPO_4 compounds had an acid reaction in water and their solubility increased when pH of the solution was increased to pH 5. Because the soil and macronutrient carrier affect the pH at soil:fertilizer interface, the solubility of nutrients in water may not necessarily be a good indication of the solubility under soil conditions. Other studies also have indicated that ulexite is relatively soluble, and may not behave as a slow-release fertilizer unless large particles are used [2]. Colemanite is less soluble, and is generally found to release B more slowly than soluble sources, with the B release rate in soil decreasing with increasing particle size [51, 56]. Overall, solubility of B minerals appears to decrease in the order: sodium borates (borax, kernite) > sodium calcium borates (ulexite) > calcium (magnesium) borates (colemanite, hydroboracite) > borosilicates (datolite, howlite). However, not only inherent solubility, but also particle size has a strong effect on the release rate of B in soil [56]. The solubility of B frits is variable, but generally low, so they need to be finely ground to be effective, and even then are more suited for maintenance fertilization than for correcting severe deficiencies [45].

6.2. Fertilizer rates and application

The B requirement of crops varies considerably, so recommended rates are crop-dependent. Also the manner of application, B status of the soil and B fertilizer source should be considered. In general, recommended rates range from 0.25 to 3 kg ha^{-1} [57]. Boron fertilizer can be either soil-applied or as a foliar spray. Soil applications are generally used on field crops, but foliar applications are commonly used to correct deficiencies in fruit trees [58]. In general, foliar fertilization has been found to be more effective than broadcast soil application [59, 60], but repeated application may be necessary because of B immobility within the plant and judicious use is required to

Table 3. The solubility of finely ground boron sources in water without pH adjustment or when pH is adjusted to 5. The BPO_4 compounds were synthesized by heating the reaction mixture of H_3PO_4 and H_3BO_3 at various temperatures for 1 h or 24 h (Results from ref [53]).

Boron source	Unadjusted pH		Adjusted to pH ~ 5
	B (mg L^{-1})	pH	B (mg L^{-1})
Sodium borate (borax)	5736 [a]	9.37	5892 [a]
Ulexite	2733	9.29	4385 [a]
Colemanite	246	9.35	3507
BPO_4			
500 °C 1 h	15.8	2.3	200
500 °C 24 h	11.2	2.5	140
800 °C 1 h	5.3	3.4	25
800 °C 24 h	4.1	3.4	20
1000 °C 1 h	1.9	3.7	5.0
1000 °C 24 h	0.2	4.4	0.5

[a]: The mineral was completely dissolved (undersaturated solution)

avoid toxicity [48]. Soil-applied B fertilizer can be either banded or broadcast. Banding is usually more effective [60], but broadcasting is often recommended to reduce the risk of seedling toxicity [48].

Boron fertilizers may exist as single-compound fertilizer, e.g., granular borax, in which case they are usually co-blended with a macronutrient fertilizer. However, there are several disadvantages of using a blend [57]. Segregation may occur during handling or application, resulting in an uneven field distribution of the B fertilizer. Also, given the high B content and low B fertilizer rates needed, the number of B-containing granules for a given area is relatively low when using a single-compound fertilizer. This may result both in higher risk of seedling toxicity, for seedlings close to a granule, and deficiency, for plants further away from the fertilizer application point. For instance, at a rate of 1 kg B ha^{-1} and with granules of circa 50 mg weight, the inter-distance between granules would be around 24 cm. It is estimated that at ten days after application, concentration close the granule (<4 cm) would be in the toxic range, while concentrations further away (>6 cm) would be in the deficient range (Figure 4a) and that it would take around a year for the fertilizer B to be evenly spread in the topsoil. These issues can to some extent be resolved by combining B with a macronutrient fertilizer [57]. When a macronutrient fertilizer is enriched with a B source to reach a concentration of 0.5% B in the fertilizer, a rate of 1 kg B ha^{-1} corresponds to an inter-distance between granules around 5 cm, and the concentrations around the granule are expected to be in the adequate range for most crops (Figure 4b). Micronutrients can be combined with the macronutrient fertilizer either by incorporation during granulation or compaction, or as a coating post-granulation. Coatings provide more flexibility than incorporation to obtain specific grades, but care must be taken to ensure the coating is homogeneous and adheres

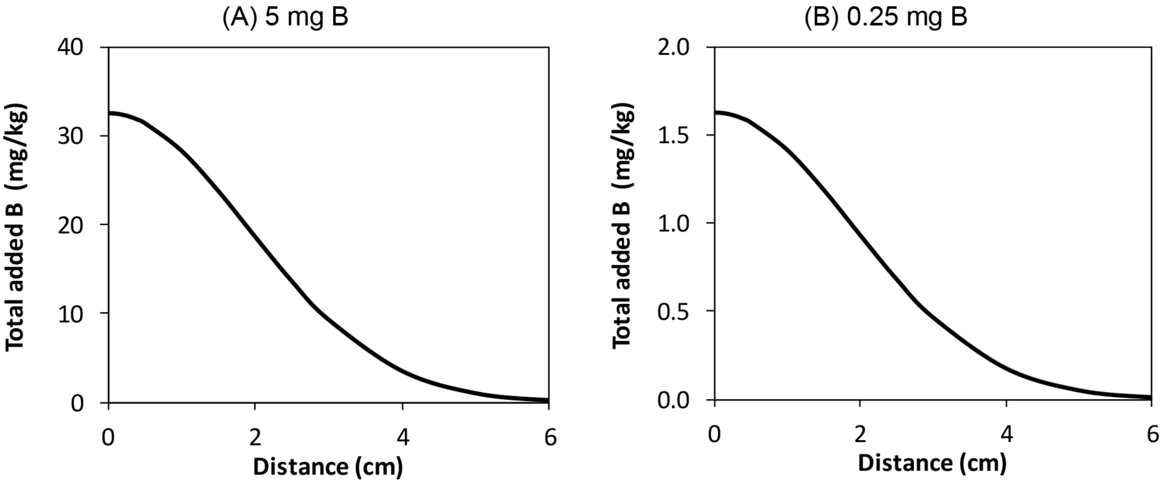

Figure 4. Estimated concentration profile of B around a fertilizer granule 10 days after application for a granule containing (A) 5 mg easily soluble B or (B) 0.25 mg easily soluble B. Note the different scales of the y-axes. The concentration profiles were modelled using the analytical solution for spherical diffusion from a point source [70], assuming a bulk density of 1.43 kg L^{-1}, volumetric water content of 0.25, tortuosity factor of 0.19, K_d of 0 (no sorption) and diffusion coefficient in water of 1.12×10^{-5} cm^2 s^{-1}.

well to the granule. In general, co-granulation is most commonly used for large-tonnage products, whereas coating is mainly used to add micronutrients to specialty fertilizers [57].

7. Advantages of slow-release fertilizers

Sodium borates are most commonly used as a B fertilizer source, but they are highly soluble, which increases both the risk of seedling toxicity and of leaching losses, which may result in deficiency later in the season. Slow-release fertilizers release the nutrients at a slower rate than fertilizers in which the nutrient is readily available and hence extend the availability to the plant [61]. Ideally, the release of a slow-release source should be slow enough to protect against leaching and seedling toxicity, but fast enough to provide nutrients in a reasonable time frame for crop growth.

7.1. Less risk of seedling toxicity

In a recent study [62], toxicity of several B sources co-granulated with MAP or MOP was assessed using a newly developed method. A granule was placed in the centre of a soil-filled Petri dish, canola was densely seeded and grown for 12 days, after which the area of the non-vegetated zone was determined (Figure 5). No B toxicity was observed around granules with 2% B as BPO_4 synthesized at high temperature. Ulexite and borax showed the highest toxicity. Colemanite also showed considerable toxicity when cogranulated with MAP, but not when cogranulated with MOP. This effect of macronutrient carrier could be explained by lower pH and high P concentrations around the MAP granule, which result in lower Ca^{2+} activity because of the precipitation of Ca phosphates, resulting in enhanced dissolution of colemanite [63]. The visual toxicity effects corresponded well with the chemical analysis of the soil in concentric circles around the soil, which showed that toxicity roughly occurred when HWB concentrations exceeded 5 mg kg^{-1} (Figure 5). Mortvedt and Osborn [64] also pointed out that high concentrations around boronated granules may result in seedling toxicity, as they found that concentrations near granules with 2% B as a soluble B source were in the toxic range for canola even at 8 weeks after application. They suggested toxicity could be prevented by decreasing B content of the granule or by using a less soluble B source. The lower risk of toxicity with slow-

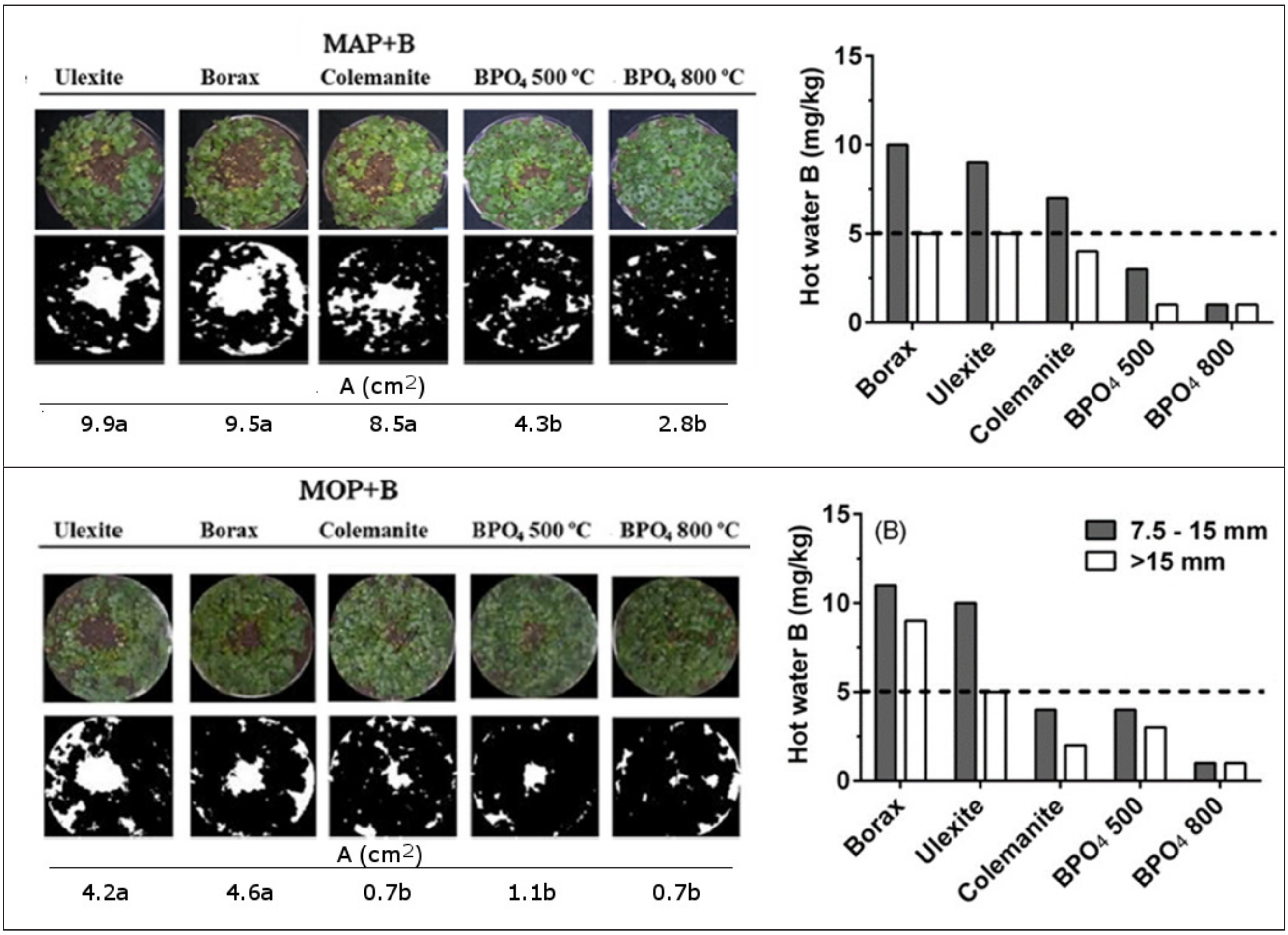

Figure 5. (Left) Pictures (original and after image processing) of Petri dishes with a granule of MAP +2% B (top) or MOP + 2% B (bottom) applied in the centre, at seven days after fertilizer application and plant seeding. (Right) The hot water-extractable B (HWB) concentrations in the same Petri dishes at 12 days after fertilizer application in the soil at 7.5-15 mm or >15 mm from the fertilizer application site. The dashed line indicates a HWB concentration of 5 mg kg^{-1}, which is considered to be toxic for many species. Results from Ref. [62].

release sources has also been demonstrated in field trials. For instance, Winsor [49] found that the yield of hairy indigo was reduced at borax rates of 22.4 kg ha^{-1} (corresponding to 2.6 kg B ha^{-1}), which was attributed to B toxicity, as visual toxicity symptoms were observed. Crop injury was much more severe with borax than with colemanite at the same rate of B.

7.2. Less leaching

The other advantage of a slow-release B source is that its gradual release more closely matches the plant demand, reducing the risk that mobile nutrients are leached away before they are required by the plant. This lower risk of leaching with slow-release sources has been demonstrated in several studies. In a laboratory study comparing B leaching from different B sources cogranulated with MAP, it was found that B from ulexite and borax had completely leached after a few pore volumes, whereas 42% or >80% was still retained in the soil for the colemanite and BPO_4 compounds respectively [63]. Saleem et al. [65] assessed leaching from borax, powdered and granular colemanite in column studies, and found that leaching losses were greatest for the borax treatment and lowest for the granular colemanite. In a field leaching study on a loamy sand [51], borax leached out of the topsoil very rapidly, while howlite leached slowly, with concentrations in the topsoils changing little over a 12-months period. Colemanite was found to be intermediate between the soluble highly sodium borate and the sparingly soluble borosilicate. Winsor [56] compared retention of borax and colemanite of various particle sizes in a sandy soil (Figure 6). He found that after 3 weeks (25 cm rainfall), only 9% of the B added as borax was recovered in the top 15 cm. Also fine colemanite (<0.4 mm) leached quite quickly, as evident from elevated B concentrations in the subsoil after 15 weeks (52 cm rainfall). Coarse colemanite, on the other hand, showed a gradual release of B and less leaching, as was evident from its persistence in the topsoil and low concentrations in the subsoil.

7.3. Adequate B supply over a longer period

Slow-release sources keep available nutrient concentrations in soil solution at a lower level than readily soluble sources, resulting in less risk of seedling toxicity and leaching loss. The nutrient level is hence sustained at an adequate level over a longer period of time. This is illustrated in Figure 7, which shows the HWB concentration in the top soil at different times after fertilizer application to a sandy soil [56]. For borax and fine colemanite, HWB concentrations were initially high, with fine colemanite even showing higher B concentrations and greater injury to native plants than borax, because B applied as borax got quickly leached to the subsoil due to heavy rains in the first weeks. The HWB concentration declined rapidly for these two sources to <0.25 mg kg^{-1}, a level that may be inadequate for many plant species, after 15 and 26 weeks for borax and fine colemanite, respectively. In

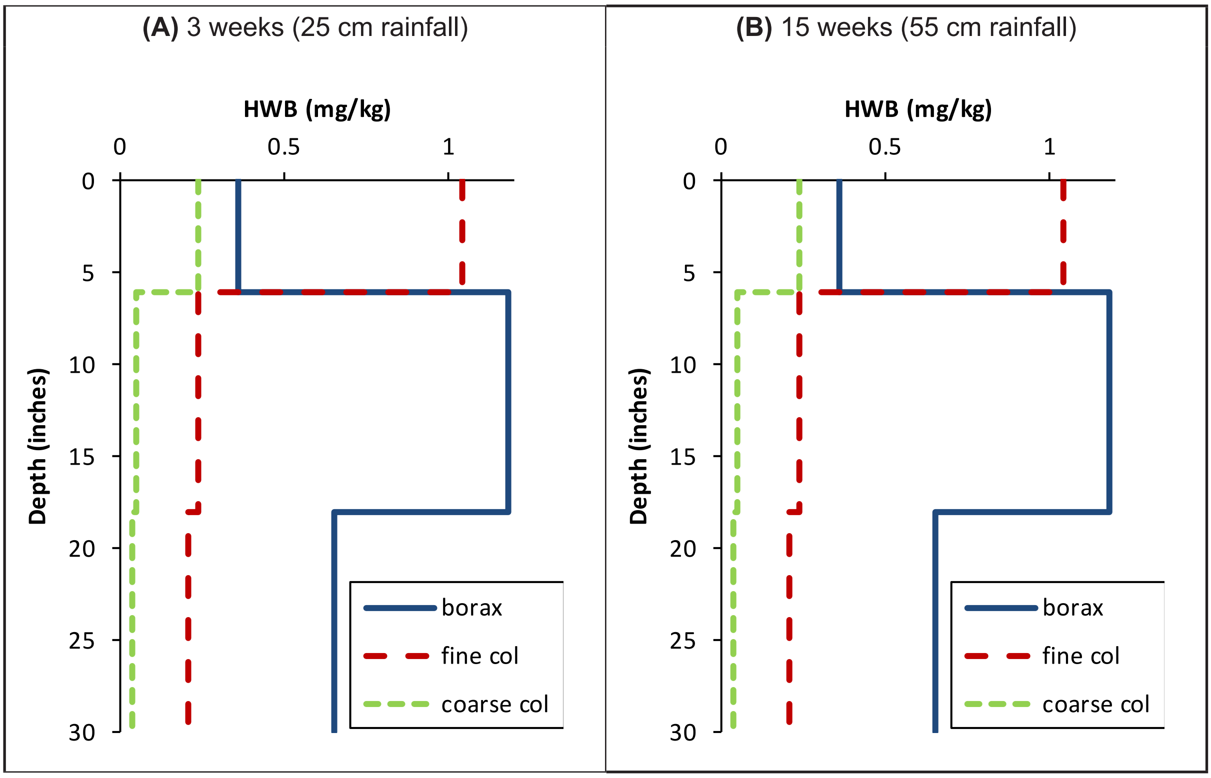

Figure 6. Concentration profiles of hot water-extractable B (HWB) at 3 weeks or 15 weeks after fertilizer application for a sandy soil treated with 6.5 kg B ha^{-1} as borax, fine colemanite (<0.4 mm) or coarse colemanite (0.8-2 mm). Graphs based on data from Winsor [56].

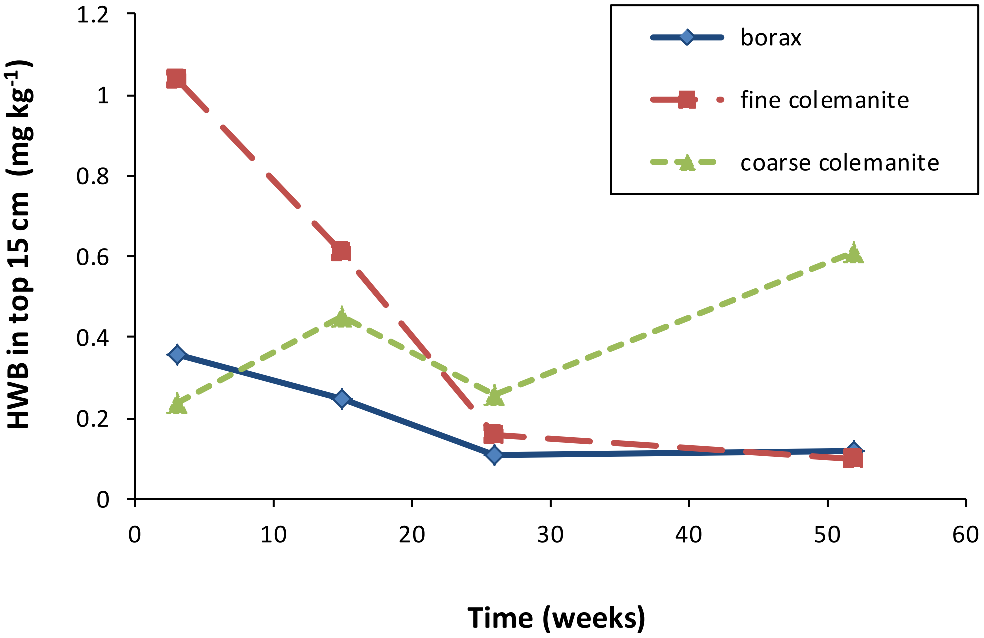

Figure 7. Concentration of hot water-extractable B (HWB) in the topsoil (0-15 cm) at different times after fertilizer application for a sandy soil treated with 6.5 kg B ha^{-1} as borax, fine colemanite (<0.4 mm) or coarse colemanite (0.8-2 mm). Graph based on data from Winsor [56].

contrast, coarse colemanite showed gradual release of B and persistence in the topsoil during 52 weeks (Figure 7). Similarly, Winsor [49] observed that colemanite (<0.8 mm) caused no injury to hairy indigo at a rates of 22 kg ha^{-1} (3.5 kg B ha^{-1}), and caused only a marginal injury at a rate of 45 kg ha^{-1} (7 kg B ha^{-1}), whereas borax at similar rates showed severe injury and strong yield reduction. In a field study assessing B supply from various B fertilizer to pine trees [66], it was observed that coarse-ground (>2 mm) ulexite and colemanite were greatly superior to borax in providing a steady, adequate supply of B to the trees.

The use of slow-release B fertilizers also extends the residual effect for subsequent crops. In silt and clay soils, even soluble B fertilizers may have a substantial residual effect because of retention of B in the soil, but in sandy and/or acid soils, B is leached easily (Figure 1) and residual effects of soluble sources are expected to be small in regions with considerable rainfall. Abat et al. [67] conducted a pot trial growing two crops of canola with regular simulated rainfall, using different B sources cogranulated with MAP applied at the start of the experiment. In the first crop, plants grown on the treatments with the most soluble sources (borax and ulexite) showed elevated tissue B concentrations, toxicity symptoms and slight yield reduction, while in the second crop, shoot B concentrations were marginal (< 20 mg kg^{-1}) and the plants displayed deficiency symptoms. In contrast, the plants grown with the less soluble sources (BPO_4) showed no toxicity or deficiency symptoms and no yield reduction in either of the crops. Saleem et al. [68] found that borax and powdered colemanite showed similar B availability for two seasons of rice on a calcareous soil, with powdered colemanite slightly better than borax in the second season, whereas granular colemanite (0.3 mm) was less effective, likely due to slow dissolution in the calcareous soil. Based on the limited literature data, it appears that relatively coarse colemanite (around 1 mm) may be a good B source on acid sandy soils, whereas finer colemanite or coarse ulexite may be a better B source on pH-neutral or alkaline soils, because of the slower dissolution of these basic ores under alkaline conditions.

Because slow-release sources prolong B availability and reduce leaching losses, they may allow to use lower rates or less frequent application of B fertilizer, provided they sustain a release that meets the plant demand. Dissolution rates of slow-release B fertilizers are dependent on soil characteristics, the B source used (inherent solubility and particle size) and the manner of application. Slightly soluble B minerals such as colemanite have been demonstrated to be suitable as slow-release B source and are relatively cheap. However, more research is needed to reliably predict release rates of B from relevant slow-release sources under field conditions. In recent years, slow-release fertilizers which use slow-release matrices or coatings have received considerable attention, mostly for nitrogen fertilizers. Similar techniques may also be applied to produce slow-release B fertilizers (see for instance ref. [54]), but so far there appear to be no published studies which assessed the effectiveness of such fertilizer under field conditions.

Acknowledgments

I gratefully acknowledge the financial support of the Mosaic Fertilizer Company. I also thank BOREN for supporting my attendance at the International Boron

Symposium in Ankara (November 2016). Furthermore, I thank Margaret Abat, Mike McLaughlin, Roslyn Baird and Rodrigo Coqui da Silva for fruitful discussions on the topic of this paper.

References

[1] Gupta U. C., Boron nutrition of crops, Advances in Agronomy, 31, 273-307, 1980.

[2] Shorrocks V. M., The occurrence and correction of boron deficiency, Plant and Soil, 193, 121-148, 1997.

[3] Nable R. O., Bañuelos G. S., Paull J. G., Boron toxicity, Plant and Soil, 193, 181-198, 1997.

[4] Oertli J., Non-homogeneity of boron distribution in plants and consequences for foliar diagnosis, Commun. Soil Sci. Plant Anal., 25, 1133-1147, 1994.

[5] Evans C. M., Sparks D. L., On the chemistry and mineralogy of boron in pure and in mixed systems: A review, Commun. Soil Sci. Plant Anal., 14, 827-846, 1983.

[6] Goldberg S., Forster H., Heick E., Boron adsorption mechanisms on oxides, clay minerals, and soils inferred from ionic strength effects, Soil Sci. Soc. Am. J., 57, 704-708, 1993.

[7] Goldberg S., Glaubig R. A., Boron adsorption on aluminium and iron oxide mineral, Soil Sci. Soc. Am. J., 49, 1374-1379, 1985.

[8] Goldberg S., Forster H., Boron sorption on calcareous soils and reference calcites, Soil Sci., 152, 304-310, 1991.

[9] Gu B., Lowe L., Studies on the adsorption of boron on humic acids, Can. J. Soil Sci., 70, 305-311, 1990.

[10] Goldberg S., Reactions of boron with soils, Plant and Soil, 193, 35-48, 1997.

[11] Keren R., Gast R., Bar-Yosef B., pH-dependent boron adsorption by Na-montmorillonite, Soil Sci. Soc. Am. J., 45, 45-48, 1981.

[12] Mezuman U., Keren R., Boron adsorption by soils using a phenomenological adsorption equation, Soil Sci. Soc. Am. J., 45, 722-726, 1981.

[13] Singh S. S., Boron adsorption equilibrium in soils, Soil Sci., 98, 383-387, 1964.

[14] Chaudhary D., Shukla L., Gupta A., Boron equilibria in soil–A review, Agricultural Reviews, 26, 288-294, 2005.

[15] Goldberg S., Lesch S. M., Suarez D. L., Predicting boron adsorption by soils using soil chemical parameters in the constant capacitance model, Soil Sci. Soc. Am. J., 64, 1356-1363, 2000.

[16] Harder H., Handbook of geochemistry, Boron, Springer, Berlin, 1974.

[17] Mertens J., Van Laer L., Salaets P., Smolders E., Phytotoxic doses of boron in contrasting soils depend on soil water content, Plant and Soil, 342, 73-82, 2011.

[18] Kabata-Pendias A., Pendias H., Trace elements in soils and plants, CRC press Boca Raton, 1984.

[19] Elrashidi M., O'Connor G., Boron sorption and desorption in soils, Soil Sci. Soc. Am. J., 46, 27-31, 1982.

[20] Couch E. L., Grim R. E., Boron fixation by illites, Clays Clay Miner., 16, 1968.

[21] Kubota J., Berger K., Truog E., Boron movement in soils, Soil Sci. Soc. Am. J., 13, 130-134, 1949.

[22] Winsor H. W., Penetration and loss of heavy applications of borax in Florida mineral soils, Soil Sci., 74, 459-466, 1952.

[23] Communar G., Keren R., Equilibrium and nonequilibrium transport of boron in soil, Soil Sci. Soc. Am. J., 69, 311-317, 2005.

[24] Bingham F., Elseewi A., Oertli J., Characteristics of boron absorption by excised barley roots, Soil Sci. Soc. Am. J., 34, 613-617, 1970.

[25] Miwa K., Fujiwara T., Boron transport in plants: Co-ordinated regulation of transporters, Ann. Bot., 105, 1103-1108, 2010.

[26] Sommer A. L., Lipman C., Evidence on the indispensable nature of zinc and boron for higher green plants, Plant Physiol., 1, 231, 1926.

[27] Bolaños L., Lukaszewski K., Bonilla I., Blevins D., Why boron?, Plant Physiol. Biochem., 42, 907-912, 2004.

[28] Brown P. H., Shelp B. J., Boron mobility in plants, Plant and Soil, 193, 85-101, 1997.

[29] Brown P., Bellaloui N., Wimmer M., Bassil E., Ruiz J., Hu H., Pfeffer H., Dannel F., Römheld V., Boron in plant biology, Plant Biology, 4, 205-223, 2002.

[30] Yau S. K., Ryan J., Boron toxicity tolerance in crops: A viable alternative to soil amelioration, Crop Sci., 48, 854-865, 2008.

[31] Gupta U., Deficiency, sufficiency, and toxicity levels of boron in crops, Boron and its role in crop production, Boca Raton: CRC Press, 137-145, 1993.

[32] Stiles A. R., Bautista D., Atalay E., Babaoğlu M., Terry, N., Mechanisms of boron tolerance and accumulation in plants: a physiological comparison of the extremely boron-tolerant plant species, *Puccinellia distans*, with the moderately boron-tolerant *Gypsophila arrostil*, Environ. Sci. Technol., 44, 7089-7095, 2010.

[33] Jin J.-y., Martens D., Zelazny L., Distribution and plant availability of soil boron fractions, Soil Sci. Soc. Am. J., 51, 1228-1231, 1987.

[34] Aitken R., Jeffrey A., Compton B., Evaluation of selected extractants for boron in some Queensland soils, Soil Res., 25, 263-273, 1987.

[35] Chaudhary D., Shukla L., Evaluation of extractants for predicting availability of boron to mustard in arid soils of India, Commun. Soil Sci. Plant Anal., 35, 267-283, 2004.

[36] Gupta U., Jame Y., Cambell C., Leyhson A., Nicholaichuk W., Boron toxicity and deficiency: a review, Can. J. Soil Sci., 65, 381-409, 1985.

[37] Bell R. W., Diagnosis and prediction of boron deficiency for plant production, Plant and Soil, 193, 149-168, 1997.

[38] Tsadilas C., Yassoglou N., Kosmas C., Kallianou C., The availability of soil boron fractions to olive trees and barley and their relationships to soil properties, Plant and Soil, 162, 211-217, 1994.

[39] Wear J. I., Patterson R., Effect of soil pH and texture on the availability of water-soluble boron in the soil, Soil Sci. Soc. Am. J., 26, 344-346, 1962.

[40] Berger K., Boron in soils and crops, Advances in Agronomy, 1, 321-351, 1949.

[41] Aubert H., Pinta M., Trace elements in soils, Elsevier, 1980.

[42] Keren R., Boron, American Society of Agronomy, Madison, WI., 1996.

[43] Keren R., Bingham F., Advances in soil science, Boron in water, soils, and plants, Springer, 1958.

[44] Jame Y., Nicholaichuk W., Leyshon A., Campbell C., Boron concentration in the soil solution under irrigation: A theoretical analysis, Can. J. Soil Sci., 62, 461-470, 1982.

[45] Mortvedt J. J., Woodruff J. R., Boron and its role in crop production, Technology and application of boron fertilizers for crops, CRC Press, Boca Raton, FL, 1993.

[46] Stormcrow, Borates Industry Report, Available at: http://www.stormcrow.ca., 2015.

[47] Brooker M., Technical Report on the Tincalayu Borax Mine, Salta Province, Argentina prepared by Hydrominex Geoscience Consulting for NI43-101, Orocobre Ltd., 2014.

[48] Martens D., Westermann D., Micronutrients in Agriculture (2nd Ed), Chap. 15: Fertilizer application for correcting micronutrient deficiencies, Soil Science Society of America, Madison, WI, 1991.

[49] Winsor H. W., Boron sources of moderate solubility as supplements for sandy soils, Soil Sci., 69, 321-332, 1950.

[50] Byers D., Mikkelsen R., Cox F., Greenhouse evaluation of four boron fertilizer materials, J. Plant Nutr., 24, 717-725, 2001.

[51] Wear J. I., Wilson C. M., Boron materials of low solubility and their use for plant growth, Soil Sci. Soc. Am. J., 18, 425-428, 1954.

[52] Ray L. F., Boron phosphate as boron source for plant life, United States Patent 3655357, 1972.

[53] Abat M., Degryse F., Baird R., McLaughlin M. J., Formulation, synthesis and characterization of boron phosphate (BPO_4) compounds as raw materials to develop slow-release boron fertilizers, J. Plant Nutr. Soil Sci., 177, 860-868, 2014.

[54] Xie L., Liu M., Ni B., Zhang X., Wang Y., Slow-release nitrogen and boron fertilizer from a functional superabsorbent formulation based on wheat straw and attapulgite, Chem. Eng. J., 167, 342-348, 2011.

[55] Bortolin A., Serafim A. R., Aouada F. A., Mattoso L. H., Ribeiro C., Macro-and micronutrient simultaneous slow release from highly swellable nanocomposite hydrogels, J. Agric. Food. Chem., 64, 3133-3140, 2016.

[56] Winsor H. W., Boron retention in Rex fine sand as related to particle size of colemanite supplements, Soil Sci., 71, 99-104, 1951.

[57] Mortvedt J. J., Micronutrients in agriculture (2nd Ed), Chap. 14: Micronutrient fertilizer technology, Soil Science Society of America, Madison, WI, 1991.

[58] Wells M. L., Conner P. J., Funderburk J. F., Price J. G., Effects of foliar-applied boron on fruit retention, fruit quality, and tissue boron concentration of pecan, HortScience, 43, 696-699, 2008.

[59] Touchton J., Boswell F., Boron application for corn grown on selected southeastern soils, Agron. J., 67, 197-200, 1975.

[60] Gupta U., Cutcliffe J., Effects of methods of boron application on leaf tissue concentration of boron and control of brown-heart in rutabaga, Can. J. Plant. Sci., 58, 63-68, 1978.

[61] Trenkel M. E., Slow-and controlled-release and stabilized fertilizers: An option for enhancing nutrient use efficiency in agriculture, International Fertilizer Industry Association (IFA), Paris, 2010.

[62] Abat M., Degryse F., Baird R., McLaughlin M. J., Boron phosphates (BPO_4) as a seedling-safe boron fertilizer source, Plant and Soil, 391, 153-160, 2015.

[63] Abat M., Degryse F., Baird R., McLaughlin M. J., Slow-release boron fertilisers: co-granulation of boron sources with mono-ammonium phosphate (MAP), Soil Res., 53, 505-511, 2015.

[64] Mortvedt J., Osborn G., Boron concentration adjacent to fertilizer granules in soil, and its effect on root growth, Soil Sci. Soc. Am. J., 29, 187-191, 1965.

[65] Saleem M., Khanif Y., Ishak Y. F., Samsuri A. W., Solubility and leaching of boron from borax and colemanite in flooded acidic soils, Commun. Soil Sci. Plant Anal., 42, 293-300, 2011.

[66] Hunter I., Will G., Skinner M., A strategy for the correction of boron deficiency in radiata pine plantations in New Zealand, For. Ecol. Manage., 37, 77-82, 1990.

[67] Abat M., Degryse F., Baird R., McLaughlin M. J., Responses of canola to the application of slow-release boron fertilizers and their residual effect, Soil Sci. Soc. Am. J., 79, 97-103, 2015.

[68] Saleem M., Yusop M. K., Ishak F., Samsuri A. W., Hafeez B., Boron fertilizers borax and colemanite application on rice and their residual effect on the following crop cycle, Soil Sci. Plant Nutr., 57, 403-410, 2011.

[69] Šimůnek J., Van Genuchten M. T., Šejna M., The HYDRUS software package for simulating two-and three-dimensional movement of water, heat, and multiple solutes in variably-saturated media, Technical manual version 1, 2006.

[70] Crank J., The mathematics of diffusion, Oxford university press, 1979.