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THE DEVELOPMENT OF NEW SLOW-RELEASE  
BORON FERTILIZERS

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## Abstract

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Boron (B) deficiency and/or toxicity have caused significant impacts on agricultural crop production worldwide. The most commonly used sources of fertilizer B are water soluble, and are therefore susceptible to leaching in high rainfall environments. This may result in insufficient supply of B for plant growth later in the crop growth cycle (e.g. flowering), when B supply is most needed. Moreover, these highly soluble sources pose an increased risk of B toxicity to seedlings just after planting. One possible way to reduce nutrient losses and avoid seedling toxicity is by using slow-release fertilizer. Slow-release fertilizers provide an effective means to overcome the low use-efficiency and problems associated with highly soluble fertilizers in soils prone to nutrient leaching.

This study has identified boron phosphate ( $\text{BPO}_4$ ) compounds as potential raw materials for incorporation into macronutrient fertilizers to produce compound fertilizers containing slow-release B. The  $\text{BPO}_4$  compounds were found to differ significantly from most commercially available B sources in terms of their physical and chemical characteristics. Boron phosphate compounds synthesized at 500 and 800 °C had low water solubility, with solubility decreasing with decreasing pH, slow kinetics of B release and B concentrations released initially from this B source by water were below the toxicity level for most crops. Products synthesized at these two temperatures were free flowing and were readily incorporated into granular mono-ammonium phosphate (MAP) granules. The solubility of other slow-release B sources, namely ulexite and colemanite, were enhanced when co-granulated with MAP due to the low pH and high P concentrations in this macronutrient fertilizer – they therefore lost their slow release characteristics when co-granulated with MAP. This limitation did not apply to  $\text{BPO}_4$  compounds where low pH and high P concentrations did not affect, or even slowed, B release.

A rapid method to screen fertilizers for possible adverse effects of high B concentrations on germinating seedlings was developed, by assessing canola (*Brassica napus* L.) germination in Petri dishes using image analysis. The MAP fertilizers co-granulated with ulexite, borax and colemanite had an adverse effect on emerging canola seedlings even at a low total B concentration in the product (0.5% B). On the other hand, no toxicity symptoms were observed with the application of MAP co-granulated with  $BPO_4$  even at higher B concentrations in the fertilizer (2.0% B). Concentrations of hot-water soluble B measured around the granule application site were in agreement with the toxicity results, with concentrations in the toxic range close to the granule for the most soluble B sources.

In plant uptake experiments examining the recovery of B by plants from the various slow-release formulations by two crops of canola, the application of co-granulated soluble B sources led to toxicity in the first crop and deficiency in the second crop. The canola shoot dry weight was increased in treatments using co-granulated  $BPO_4$  products compared with the unfertilized control for both crops. This result suggested that a single application of a macronutrient fertilizer containing co-granulated  $BPO_4$  would be an effective slow-release B fertilizer for several cropping cycles.

In summary, co-granulated  $BPO_4$  products have potential as sources of slow-release B for incorporation into macronutrient fertilizers designed for high rainfall environments. This research work could have important implications for future B fertilizer development.

## Declaration

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I certify that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution, and to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. In addition, I certify that no part of this work will, in the future, be used in a submission for any other degree or diploma in any university or other tertiary institution without the prior approval of the University of Adelaide and where applicable, any partner institution responsible for the joint-award of this degree.

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(Margaret Abat)

Date: 1<sup>st</sup> December 2014



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## Conference Proceedings

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A slow-release safe source of fertiliser boron to mitigate boron deficiency in high rainfall environments. In Proceedings of the 5<sup>th</sup> Joint Australian and New Zealand Soil Science Conference, Hobart, Tasmania, 2 – 7 December 2012, p 533.
3. Margaret Abat, Michael J McLaughlin, Fien Degryse, Roslyn Baird. (2013)  
Boron phosphate (BPO<sub>4</sub>) as safe-seedling and slow-release boron fertilizer. In Proceedings XVII International Plant Nutrition Colloquium (IPNC) and Boron Satellite Meeting 2013, Istanbul, Turkey, 17 – 22 August 2013. p 943

## List of Abbreviations

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Å	Angstrom
Al	Aluminium
ANOVA	Analysis of variance
AR	Analytical reagent
As	Arsenic
B	Boron
B(OH) <sub>3</sub>	Boric acid
B(OH) <sub>4</sub> <sup>-</sup>	Borate ion
BPO <sub>4</sub>	Boron phosphate
°C	Degree Celcius/centigrade
Ca	Calcium
Ca <sub>2</sub> B <sub>6</sub> O <sub>11</sub> .5H <sub>2</sub> O	Calcium borate/colemanite
CaCl <sub>2</sub>	Calcium chloride
CaCO <sub>3</sub>	Calcium carbonate
CaMgB <sub>6</sub> O <sub>11</sub> .6H <sub>2</sub> O	Hydroboracite
CEC	Cation exchange capacity
cm	Centimetre
CSIRO	Commonwealth Scientific and Industrial Research Organization
Cu	Copper
d	Day
DAP	Diammonium phosphate
DCPD	Dicalcium phosphate dihydrate
DI	Deionized water
erfc	Complementary error function
FC	Field capacity
Fe	Iron
g	Gram
h	Hour
H <sup>+</sup>	Hydrogen ion
ha	Hectare
H <sub>3</sub> BO <sub>3</sub>	Boric acid
HCl	Hydrochloric acid
HgCl <sub>2</sub>	Mercuric chloride
HNO <sub>3</sub>	Nitric acid
H <sub>3</sub> PO <sub>4</sub>	Phosphoric acid
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid
ICP-OES	Inductively coupled plasma – optical emission spectroscopy
K	Potassium
K <sub>d</sub>	Soil-solution distribution coefficient
K <sub>sp</sub>	Solubility product constant
kg	Kilogram
L	Litre
LSD	Least significant difference
M	Molar
MAP	Mono-ammonium phosphate
Mg	Magnesium
mg	Milligram

min	Minute
mg/kg	Milligram per kilogram
mg/L	Milligram per litre
mM	Millimolar
mL	Millilitre
Mn	Manganese
Mo	Molybdenum
μL	Microlitre
μM	Micromolar
N	Nitrogen
Na	Sodium
NaCaB <sub>5</sub> O <sub>9</sub> .8H <sub>2</sub> O	Sodium-calcium borate/ulexite
NaOCl	Sodium hypochlorite
NaOH	Sodium hydroxide
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .5H <sub>2</sub> O	Sodium tetraborate pentahydrate
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> .10H <sub>2</sub> O	Sodium tetraborate decahydrate
NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	Mono-ammonium phosphate
NH <sub>3</sub>	Ammonia
OH <sup>-</sup>	Hydroxyl ion
P	Phosphorus
<i>P</i>	Probability
pH	The negative log of hydrogen ion activity, (-log[H <sup>+</sup> ])
pK <sub>a</sub>	The negative log of acid dissociation constant
PV	Pore volume
RCF	Relative centrifugal force
RCBD	Randomized complete block design
s	Second
S	Sulfur
SD	Standard deviation
Si	Silicon
SSP	Single superphosphate
TSP	Triple superphosphate
XRD	X-ray diffraction
Zn	Zinc

## 1.1 Background

Boron (B) is one of the essential micronutrients required for normal plant growth and development (Gupta, 1979). Boron deficiency is a widespread problem and often occurs in coarse-textured soils and in high rainfall regions (Shorrocks, 1997). Although less prevalent than B deficiency, B toxicity also occurs, mostly in arid or semi-arid areas because of high B concentrations in the soil and from the addition of B in irrigation water (Gupta, 1983). Boron toxicity may also occur because of over- or uneven application of B fertilizers. Both deficiency and toxicity of B can cause reductions in crop yield and/or impair crop quality (Cartwright et al., 1984; Gupta et al., 1985).

The requirement of plants for B is higher during the reproductive growth or seed production stage than it is in the vegetative stage. Severe B deficiency and/or toxicity in plants may produce very little or no yield at all (Mozafar, 1993). As a result of the general immobility of B, which is a characteristic of most plant species, and the higher B requirements during reproductive stages of growth, plants require a continuous supply of B from soil for their entire growth cycle.

The most commonly used B fertilizers to correct B deficiency are water soluble, e.g. sodium borates (borax) or boric acid. A disadvantage of soluble B sources is their low fertilizer use-efficiency due to leaching losses after application and before plant uptake (Mortvedt, 1994). Moreover, these highly soluble sources pose an increased risk of B toxicity to seedlings just after planting (Kmecl and Bukovec, 1999). Less soluble B minerals such as colemanite and ulexite have been used as slow-release B sources to overcome problems due to B toxicity and

leaching, but it has been found that they behave similarly to borax when incorporated with macronutrient fertilizers (Wear and Wilson, 1954).

Other B sources may have potential as a slow-release B source. Lewis and Wear (1972) and Ray (1972) suggested the use of pure or spent  $BPO_4$  as a slow-release B source for plant growth, but very little detail was provided regarding B release characteristics and the compatibility of this mineral with macronutrient (nitrogen (N), phosphorus (P) and potassium (K)) fertilizers. The relatively high B content (10%) in  $BPO_4$  and its low solubility should make it an efficient slow-release B fertilizer source (Magda et al., 2010), particularly for incorporation with macronutrient fertilizers.

This thesis investigated the suitability of  $BPO_4$  compounds for co-granulation with macronutrient fertilizers, examined the release of B from these materials, the potential for seedling toxicity, and finally the ability to supply B over an extended period to plants. This information may assist in developing novel slow-release B fertilizers which can provide effective, environmentally friendly and relatively inexpensive alternatives to fertilization with soluble B sources.

## **1.2 Thesis Outline**

This thesis is organized into seven chapters. A review of the literature pertaining to B in soils and plants, and B fertilization of crops is given in Chapter 2. The experimental chapters (Chapters 3, 4, 5 and 6) in this thesis have been written in manuscript style for publication in peer reviewed journals.

The synthesis and physio-chemical characteristics of  $BPO_4$  as a raw material for development of slow-release B fertilizer are reported in Chapter 3. The effects of manufacturing conditions on the behavior of  $BPO_4$  are described, with the aim to formulate  $BPO_4$  with suitable characteristics for inclusion in macronutrient fertilizers.

Due to the problems associated with separate applications of pure B fertilizers and bulk-blended B fertilizers, Chapter 4 describes the granulation of  $BPO_4$  compounds with a macronutrient fertilizer, namely mono-ammonium phosphate (MAP). Commercially available B sources such as borax, ulexite and colemanite were also co-granulated with MAP for comparison. The kinetics of B release from these products and other characteristics of the co-granulated products are presented.

In Chapter 5, a novel toxicity test is described to examine seed germination and seedling toxicity of soil-applied fertilizer products, and the co-granulated B formulations sources were assessed using this technique.

In Chapter 6 a pot experiment is described which examined the long-term B supply characteristics of the co-granulated products for canola growth under simulated high leaching conditions. The residual value of the fertilizers to a second canola crop was also investigated.

In Chapter 7, general conclusions are presented along with implications of the findings and suggestions for future research.

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**2.1 Introduction**

Most boron (B) in the soil originates from soil minerals derived from sedimentary rocks and/or igneous rocks (Evans and Sparks, 1983; Kot, 2009). However, the B in the rock is not available to plants and most of the plant-available B comes from the decomposition of soil organic matter and from B adsorbed and precipitated onto the surfaces of soil particles (Bingham, 1973).

**2.2 Geochemistry of Boron**

Boron is a member of the subgroup III of metalloids in the Periodic Table and has intermediate properties between metals and non-metals (Marschner, 1986). It has an atomic number of five and oxidation state of +3 in most compounds (Evans and Sparks, 1983). However, B can only form covalent bonds because of its small size (ionic radius = 0.23 Å) and high ionic potential (Parks and Edwards, 2005). Boron has only two stable isotopes in nature. These have an atomic mass of 10 and 11 and occur in a 20:80 ratio, resulting in an average atomic mass of 10.81 g/mol (Parks and Edwards, 2005).

**2.2.1 Boron in minerals**

Boron in nature is found in many silicate minerals and can be classified into borosilicates, and hydrous/anhydrous borates (Parks and Edwards, 2005). Total B concentration in soil is dependent on its parent material and the degree of weathering; with values ranging from 1 to 270 mg B/kg (Barber, 1995). Clay and organic soils have higher B content than sandy soils (Kabata-Pendias, 1992). Some of the common classes of B-containing minerals and their chemical formulae are shown in Table 1.

Table 1 Boron-containing minerals.

<b>Class</b>	<b>Mineral names</b>	<b>Chemical formula</b>
Complex borosilicates	Tourmaline	$\text{Na}(\text{Mg,Fe,Mn,Li,Al})_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH,F})_4$
Hydrous borates	Axinite	$(\text{Ca,Mn,Fe})_3\text{Al}_2\text{BO}_3\text{Si}_4\text{O}_{12}(\text{OH})$
	Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
	Kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
	Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
	Ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
Anhydrous borates	Ludwigite	$\text{Mg}_2\text{FeBO}_5$
	Kotoite	$\text{Mg}_3(\text{BO}_3)_2$

Adapted from Krauskopf (1972).

The complex borosilicates and anhydrous borates are high-temperature minerals, whereas hydrous borates are low-temperature minerals (Krauskopf, 1972). Tourmaline, which is highly resistant to weathering, is the most common of the high-temperature B minerals (Evans and Sparks, 1983). Tourmaline contains approximately 3% B and is virtually insoluble (Goldberg, 1997). Because of its low solubility, addition of finely ground tourmaline to soil has failed to provide sufficient B to alleviate B deficiency of crop plants (Fleming, 1980).

Hydrated borates are formed originally as chemical deposits in saline lakes (Christ et al., 1967) and can be altered by changes in temperature after deposition (Krauskopf, 1972). Hydrated sodium borates (borax) form from lakes that have a high pH and are high in sodium (Na) and low in calcium (Ca) content, whereas hydrated sodium-calcium borates (ulexite) form from lakes of higher Ca content (Goldberg, 1993) (Figure 1).

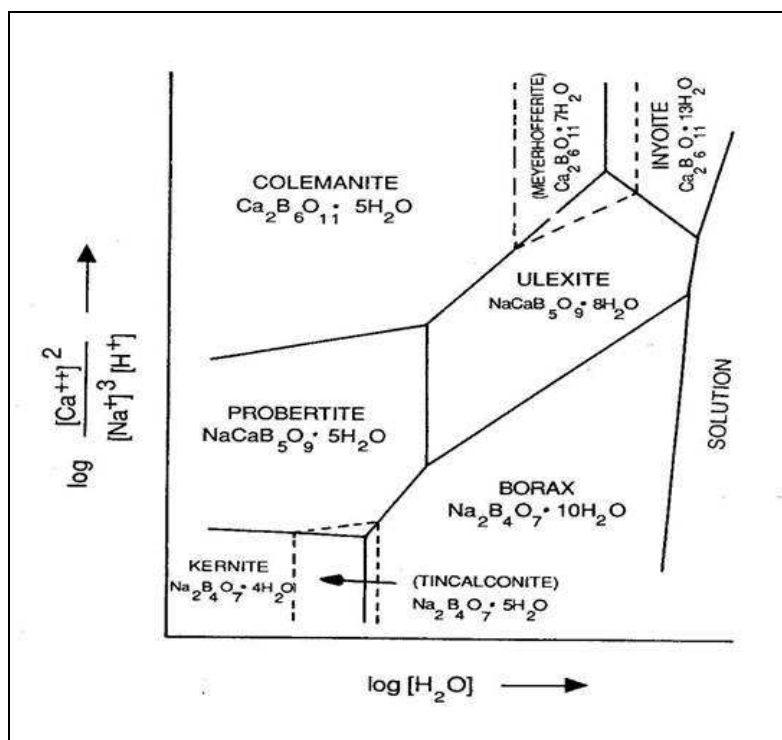


Figure 1 Schematic plot of the phase relations in the borate mineral assemblages system (Christ et al., 1967).

The B content of phyllosilicate clay minerals (Table 2) is distinctly higher than that of most other minerals (Harder, 1974). This is due to their layered structure which allows B to lie within the tetrahedral layer, lending stability (B becomes fixed) through a weak ionic bond (Couch and Grim, 1968; Fleet, 1965). To explain the irreversibility of B adsorption, Harder (1974) suggested that B incorporates into illite and chlorite lattices by substituting for tetrahedral silicon (Si) and aluminium (Al) ions. The mechanism of B sorption by illite is suggested to occur in two steps. Initially B adsorbs chemically as borate onto the particle edges of illite and subsequently migrates and incorporates into tetrahedral sites replacing structural Al and Si (Couch and Grim, 1968).

Table 2 Boron concentrations of phyllosilicates.

<b>Mineral</b>	<b>Boron concentration (mg/kg)</b>
Muscovite	10 - 500
Biotite	1 - 6
Illite	100 - 2000
Montmorillonite	5 - 200
Kaolinite	10 - 30
Chlorite	≤ 50

Source: Boron in Handbook of Geochemistry (Harder, 1974).

### 2.2.2 Boron in solution

Boron occurs in aqueous solutions as boric acid,  $B(OH)_3$  and borate anions,  $B(OH)_4^-$  (Evans and Sparks, 1983). Boric acid is a very weak, monobasic acid that acts as a Lewis acid by accepting a hydroxyl ion ( $OH^-$ ) to form the  $B(OH)_4^-$  (Goldberg, 1993):



The equilibrium constant for the hydrolysis reaction of  $B(OH)_3$  is  $5.75 \times 10^{-10}$  or  $pK_a = 9.24$  at 25 °C (Basset, 1980). Thus, below pH 9.24, the uncharged species is predominant, while above pH 9.24, the borate anion is predominant.

Boron is unique among the essential mineral nutrients because it is the only element that is normally present in soil solution as a non-ionized molecule over the pH range suitable for plant growth (Gupta, 1993a). At B concentrations  $\leq 0.025$  M, only mononuclear B species;  $B(OH)_3$  and  $B(OH)_4^-$  are present (Cotton and Wilkinson, 1980). When B concentration in solution is above 0.025 M, polyborate species such as  $B_2O(OH)_5^-$ ,  $B_3O_3(OH)_4^-$  and  $B_4O_5(OH)_4^{2-}$  are formed (Evans and Sparks, 1983).

In saline waters, borate may form ion pairs with  $\text{Na}^+$ , magnesium ( $\text{Mg}^{2+}$ ) and  $\text{Ca}^{2+}$ , but even under these conditions, these complexes are only a minor fraction of total B in solution (Table 3) (Keren and Bingham, 1985).

Table 3 Distribution of B species in simulated irrigation waters expressed as a percentage of total B in solution<sup>a</sup>.

pH	$\text{H}_3\text{BO}_3$	$\text{B}(\text{OH})_4^-$	$\text{NaB}(\text{OH})_4^0$	$\text{CaB}(\text{OH})_4^+$	$\text{MgB}(\text{OH})_4^+$
7.0	99.0	0.9	< 0.1	< 0.1	< 0.1
8.4	79.9	17.9	0.8	0.7	0.7
9.2	39.2	55.3	2.4	0.9	2.2

<sup>a</sup> Irrigation water composition: B = 0.3 mM,  $\text{Na}^+$  = 45 mM,  $\text{Ca}^{2+}$  = 2.5 mM,  $\text{Mg}^{2+}$  = 2.5 mM,  $\text{Cl}^-$  = 50 mM, and  $\text{CO}_3^{2-}$  = 2.5 mM (Keren and Bingham, 1985).

### 2.2.3 Boron speciation in soil

Plants obtain B mainly from the soil solution (Hatcher and Bower, 1959). Therefore, it is important to determine B concentration in soil solution when assessing the plant response to soil B. However, soil adsorption sites may release B into solution or adsorb B, depending on the affinity of the soil for B and changes in the solution B concentration (Gupta et al., 1985; Keren and Bingham, 1985). The adsorbed pool of B acts as a buffer against sudden changes in solution B (Leyshon and Jame, 1993). Thus, in assessing B availability and plant response to soil B, it is important not only to consider the B concentration and speciation in the liquid phase, but also in the solid phase of the soil.

The pool of metal in the solid phase of the soil, which is capable of immediately buffering the metal ion activity in the soil solution, may be functionally described as 'labile', 'available' or 'reactive' (Young et al., 2006). This labile solid-phase pool includes B that is adsorbed on phyllosilicate clays (Goldberg et al., 1993), on variable charge oxides and hydroxides (Goldberg and Glaubig, 1985), on carbonate minerals (Goldberg and Forster, 1991), or associated with organic matter (Gu and Lowe, 1990). Ligand exchange with reactive surface

hydroxyl groups has been suggested as the mechanism of B adsorption on Al and iron (Fe) oxides (Sims and Bingham, 1968). Non-labile forms include B that replaced  $Al^{3+}$  or  $Fe^{3+}$  in hydroxides or  $Si^{4+}$  in the tetrahedral sheets of phyllosilicate clays via isomorphous substitution and B in primary minerals, such as tourmaline, or secondary minerals, such as colemanite (Hingston, 1964). The availability of B and transformations among different soil B species are dependent on factors such as pH, organic matter, clay minerals, Al and Fe oxides, carbonate content and tillage management of the soils (Jin et al., 1987; Mandal et al., 2004; Tsadilas et al., 1994).

Soil reaction or soil pH is one of the most important factors affecting the availability of B in soils for plants (Goldberg et al., 1993). Boron adsorption in soil is weak, but increases with increasing solution pH, reaching an adsorption maximum around pH 8 to 9, and decreases with further increase in solution pH (Goldberg and Su, 2005; Keren and Bingham, 1985; Keren and Sparks, 1994).

The amount of B in soil solution is usually controlled by B adsorption-desorption reactions (Goldberg et al., 1993). Boron desorption in soils has been investigated, although to a lesser extent than B adsorption (Biggar and Fireman, 1960; Elrashidi and O'Connor, 1982; Okazaki and Chao, 1968; Wild and Mazaheri, 1979). Conflicting information on the reversibility of B adsorption exists in the literature. For some soils the desorption isotherm corresponds closely to the adsorption isotherm (Elrashidi and O'Connor, 1982; Wild and Mazaheri, 1979). For other soils, irreversible sorption has been observed. The apparent irreversibility of B sorption has been attributed to conversion of readily desorbable monodentate B surface complexes into less readily desorbable bidentate complexes, incorporation of B into tetrahedral sites of clay minerals, and B diffusion into particle interiors (Goldberg and Su, 2005; Yin et al., 1997). Hysteresis tends to be greater at high B concentrations and much of the irreversibly

sorbed B can be desorbed with repeated water extractions (Gupta et al., 1985), indicating that the B is not truly fixed.

The values for the soil-solution distribution coefficient ( $K_d$ ) for B are small, up to 10 L/kg at most (Goldberg et al., 2000). As a result of this weak sorption, B is highly mobile in the soil, making it susceptible to leaching (Goldberg, 1997). In high rainfall areas or humid regions, B added in fertilizer is therefore subject to leaching which often leads to insufficient B supply from soil for plant uptake later in the crop growth cycle when B requirements are higher (Berger, 1949; Broschat, 2007; Gupta et al., 1985).

### **2.3 Boron in Plant Nutrition**

Boron is among the essential micronutrients without which plants cannot complete their life cycle (Marschner, 1986). Adequate B nutrition is critical for high yields and quality of crops. Deficiencies as well as toxicities of B result in many anatomical, biochemical and physiological changes in plants (Berger, 1949). In most plant species, B has restricted mobility as indicated by the symptoms of deficiency and toxicity between plant organs (Brown and Shelp, 1997). However, in some plant species that produce significant amounts of sorbitol (*Pyrus*, *Malus* and *Prunus* genera), B in the phloem is mobile due to the formation and transport of B-sorbitol complexes (Brown and Hu, 1996). Due to B immobility within the plant, it is even possible for toxic B concentrations (in old leaves) and deficient B concentrations (in young leaves) to occur in the same plant, if B supply was high during early growth and deficient later on (Oertli, 1994). Thus, a stable and continuous B supply is necessary to have adequate B supply throughout the whole plant cycle.

#### **2.3.1 The function of boron in plants**

Boron is important in cell division and is a necessary component of the cell wall structure (Camacho-Cristobal et al., 2008). Boron is essential in the actively growing regions of plants, such as root tips and for new leaf and bud development (Bell, 1997). Boron also plays an

important role in the synthesis of proteins and enzymes (Berger, 1949). Boron increases flower production and retention, pollen tube elongation, and seed and fruit development (Gupta et al., 1985).

Boron increases the rate of sugar translocation in mature plant leaves to the plant growing parts (Berger, 1949). Boron deficiency decreases the amount of chloroplasts, inhibits their development and reduces photosynthesis (Reisenauer et al., 1973). Boron affects carbohydrate metabolism significantly. Optimal B supply has a positive effect on chlorophyll contents, and results in higher efficiency and rate of photosynthesis, and enhanced translocation of photosynthesis products (Reisenauer et al., 1973).

### **2.3.2 Boron uptake by plant roots**

Plant roots absorb B from the soil solution (Keren and Bingham, 1985). Boric acid, the uncharged molecule, is the main chemical form of B taken up by plants (Marschner, 1986). The transport mechanism of B uptake by roots to the cell from the soil solution remains unclear, with substantial evidence for both passive and active transport occurring in plants (Fitzpatrick and Reid, 2009).

Under conditions of adequate or relatively high  $B(OH)_3$  supply,  $B(OH)_3$  absorption by roots is mediated through a passive process that involves B diffusion across the lipid layer (Brown and Shelp, 1997; Tanaka and Fujiwara, 2008). Boric acid exists mainly as an uncharged molecule and has an estimated lipid permeability coefficient of  $4 \times 10^{-6}$  cm/s (Raven, 1980). However, the permeability of B through plant membranes may be much lower than this estimated value. Dordas et al. (2000) found that in vesicles prepared from purified plasma membranes of squash (*Cucurbita pepo*), the permeability coefficient was only  $3 \times 10^{-7}$  cm/s. These results imply that passive diffusion across the lipid bilayer is only significant when the concentration gradient is high (high B supply) and indicates the need for membrane proteins to satisfy a plant's demand for  $B(OH)_3$  under low B conditions (Tanaka and Fujiwara, 2008).



Other physiological studies have revealed energy-dependent active transport against concentration gradients in B transport systems, particularly in low B conditions. Dannel et al. (2000) demonstrated the transport of  $B(OH)_3$  against a concentration gradient in sunflower. They found that concentration of tracer  $B(OH)_3$  ( $^{10}B$ ) was the highest in xylem exudates, followed by root cell sap and then external solution in sunflower (*H. annas*) plants grown under low B conditions (1  $\mu M$ ). In contrast, the concentration of tracer  $^{10}B$  was not significantly different between these solutions when the plants were grown under high B conditions (100  $\mu M$ ), indicating that active transport mechanisms exist in both processes of uptake and xylem loading and that these mechanisms are induced by low B conditions. Stangoulis et al. (2001) also demonstrated that a high-affinity B transport system occurred under low B supply in charophyte algae (*Chara coralina*). In rice, the B transporter OsBOR1 has been suggested to be involved in the efficient uptake of B into root cells under B deficiency (Tanaka and Fujiwara, 2008).

#### **2.3.4 Boron toxicity**

In arid zone soils, B toxicity occurs as a result of naturally high levels of water-soluble B in the soil or as a result of addition of large amounts of B in irrigation water (Nable et al., 1997). In saline soils, improper or lack of drainage leads to excessive concentrations of B in the soil solution (Goldberg, 1997). Nable et al. (1997) reported that soils containing more than 5 mg B/kg of hot water soluble B are likely to cause B toxicity to many agronomic crops. In irrigation water, B concentration should be between 0.3 and 4.0 mg B/L, depending on the crop type and soil characteristics (Keren and Bingham, 1985).

Boron requires special attention among the essential nutrients because the need for B by plants is relatively small and the range between deficiency and toxicity is narrow (Krishnasamy et al., 2005). The optimal range of B concentrations in nutrient solution, in which plants suffer neither toxicities nor deficiencies, is generally between 0.3 and 1.0 mg

B/L (Asad et al., 2001). Even though the effects of B deficiency and toxicity have been reported in many publications, confusion still exists in defining B limits for plant growth in soil. Gupta et al. (1985) characterized crop response as a function of soil solution B (Figure 2). Francois (1984) reported that each unit increase in soil solution B (in mg B/L) above the threshold value of 5.7 mg B/L reduced tomato yield by 3.4%. A decrease of 10% (EC10 values) in barley root growth has been reported when soil solution B concentrations exceeded values between 16 and 59 mg B/L across different soils (Mertens et al., 2011).

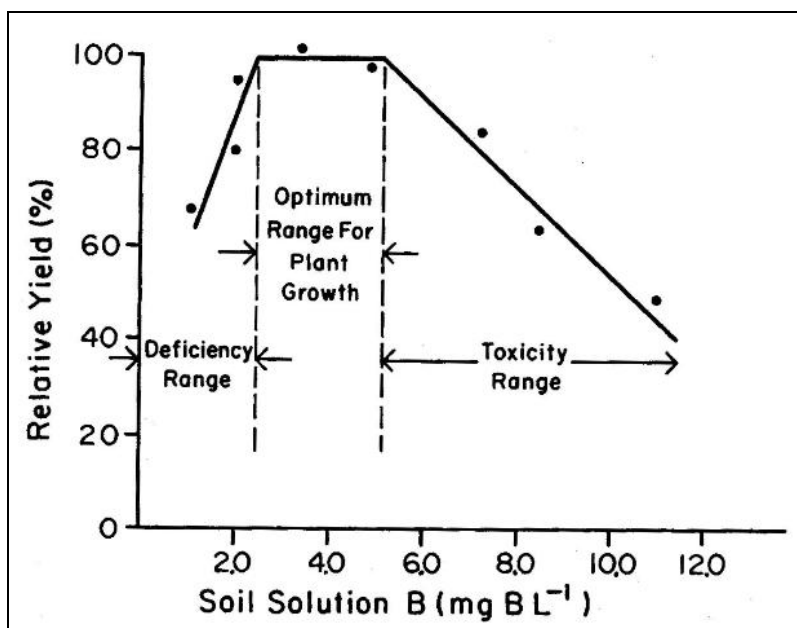


Figure 2 Relative yields as influenced by soil solution boron (Gupta et al., 1985).

### 2.3.5 Boron deficiency

Boron deficiency is a widespread problem for crop production. There are only a few but relatively large regions which have been mapped in the world where B deficiency occurs frequently in crops (Figure 3) (Shorrocks, 1997). Elsewhere, B deficiency exists in relatively small areas and is more dependent on local conditions and type of crops grown (Shorrocks, 1997). Boron deficiency has a significant negative impact on agricultural production because a deficiency of B inhibit growing tissues, specifically the productive structure of growing plant (Brown et al., 2002).

Both growth and quality of eucalyptus trees in southern China (McBride, 1997) and pine trees in southeast Australia (Hopmans and Flinn, 1984) have been severely affected by B deficiency. It has been reported that deficiency of B in plants causes sterility in wheat and mustard in Bangladesh (Ahmed and Hossain, 1997; Jahiruddin et al., 2005). Increased incidence of panicle sterility and a lower number of productive tillers per plant are major causes of yield reduction in rice in B-deficient soils of Pakistan (Goldberg, 1993).

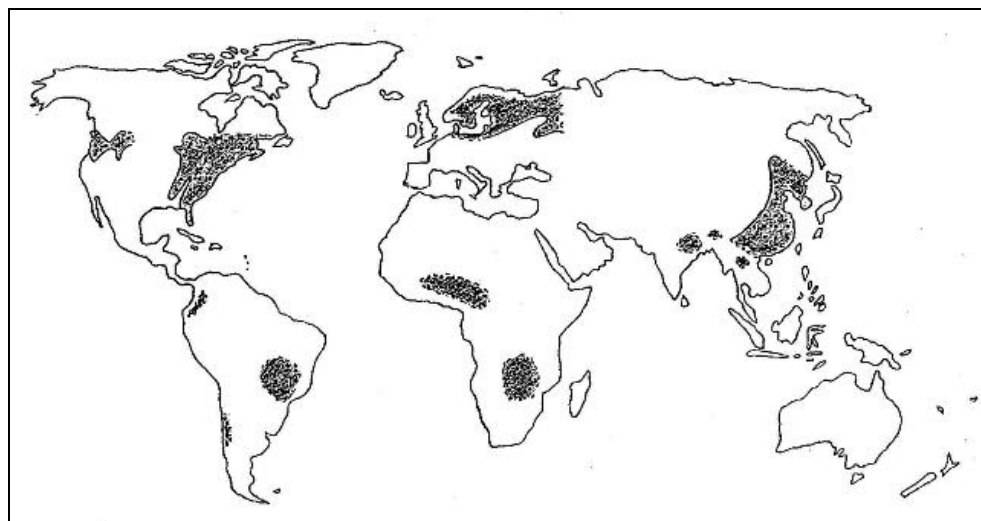


Figure 3 World most prominent B deficiency areas (Shorrocks, 1997).

Boron deficiency has been observed in light-textured acidic soils, in soils containing high amounts of calcium carbonate ( $\text{CaCO}_3$ ) or Al/Fe oxides and hydroxides and also in soils of low organic matter content (Keren and Bingham, 1985; Mandal et al., 2004). The liming of acid soils also can trigger temporary B deficiency because of increased B adsorption resulting from an increase in soil pH (Reisenauer et al., 1973). To improve crop growth farmers have used large amounts of B fertilizers over many decades (Shorrocks, 1997). However, only a small fraction of the B fertilizer applied is available for plant uptake because it is weakly sorbed by the soil and leaches easily (Shorrocks, 1997).

Hot water extraction has been used as a measure of available B in soil for plant uptake. Eguchi and Yamada (1997) studied the relationship between hot-water extractable B concentration in soil and B deficiency symptoms and tissue concentrations in celery (*Apium*

*graveolens*) and Chinese cabbage (*Brassica campestris pekinensis*). Boron deficiency symptoms appeared when the hot-water soluble B concentration in the soil was less than 0.3 mg B/kg for celery and less than 0.4 mg B/kg for Chinese cabbage. When the hot water soluble B concentration was between 0.3 and 0.5 mg B/kg, B deficiency appeared in about 50% of the crops. No B deficiency symptoms were observed in any of the celery and Chinese cabbage crops at hot water soluble B concentrations above 0.5 mg B/kg (Eguchi and Yamada, 1997).

The concentrations of B in plant tissue can be used to help diagnose deficiency or toxicity (Bell, 1997). The concentration of B in plant leaves may vary from 2 to 3875 mg B/kg (Kabata-Pendias, 1992). In general, tissue concentrations less than 15 or 20 mg B/ kg dry matter are associated with deficiency, while concentrations above 200 mg B/kg are considered toxic to plants (Reuter and Robinson, 1997). However, in some crops, the range between deficiency and toxicity can be narrower than this. For example, the critical deficiency concentration for pea is 50 mg B/kg in leaves while the critical toxicity concentration is 90 mg B/kg (Reuter and Robinson, 1997).

## **2.4 Boron Fertilization**

### **2.4.1 Use of boron fertilizers**

In the past 30 years, research on plant B nutrition has progressed significantly and the application of B fertilizer has become a standard measure in many B-deficient regions. Boron fertilizer is added to the soil in the form of very soluble to less-soluble B compounds such as sodium borate, ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ), hydroboracite ( $\text{CaMgB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$ ) and colemanite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ) (Wear and Wilson, 1954).

As a general guideline for B fertilizer recommendations, when the hot-water soluble B in soil is less than 0.5 mg B/kg, deficiency is likely to occur and all crops are to be treated with B; when it is 0.5–1.0 mg B/kg, deficiency may appear and “insurance dressings” are to be

considered; when it is more than 1.0 mg B/kg, deficiency is unlikely and B treatment is not necessary; and when it is 3–5 mg B/kg, crops may be poisoned from excess B (Berger, 1949; Gupta, 1979; Keren and Bingham, 1985; Nable et al., 1997). Since there is only a relatively small range between toxic and deficient supply, careful application of B fertilizer is necessary.

Many studies have been conducted to investigate the effect of B fertilization on crops grown on soils deficient in B. In fertilizer schedules, inclusion of B often determines the success or failure of crops (Dwivedi et al., 1990). For example, B application at the rate of 2.9 kg B/ha (as borax) significantly increased rapeseed yield (Chen et al., 1997). Boron application also has increased the yield of mulberry by 20% and improved its quality due to the increased total amino acid content in the leaf (Chen et al., 1997). A field experiment on the effects of micronutrients on mung bean (*Vigna radiata*) showed a 14% increase in seed yield over the control by application of 2.5 kg B/ha (Ahmed and Hossain, 1997). Increased grain yield (19%) in wheat by application of 4 kg B/ha was observed on a silt loam soil with low hot-water extractable B concentration of 0.25 mg B/kg (Asad and Rafique, 2000).

#### **2.4.2 Methods of boron application**

The requirement of crops for fertilizer B varies greatly between plants, soil, climatic conditions and method of application (Berger, 1949; Mortvedt and Woodruff, 1993). Only about 0.5 to 3.0 kg B/ha is required to promote the health and yields of numerous crops (Shorrocks, 1997). The method of B fertilizer application used to date are band application, broadcast or foliar spray (Mortvedt and Woodruff, 1993). Both broadcast and band applications to soil are recommended, depending upon the crop and soil conditions (Mortvedt and Woodruff, 1993). Band application may result in greater efficiency of applied B than that of broadcasting (Mortvedt and Woodruff, 1993). Higher B concentrations in rutabaga (*Brassica napobrassica* L.) leaves were reported when B was applied at 1.12 kg/ha in bands

than when applied broadcast at 2.24 kg/ha (Gupta and Cutcliffe, 1978). Greater B uptake when B is applied in bands is likely due to the fact that a large quantity of the available nutrient is concentrated in the zone that is immediately accessible to the plant roots (Gupta and Cutcliffe, 1978). However, banding has higher risk of inducing toxicity. The application of B to seeds, or even application in close proximity to the seed, is not advisable as this can lead to B toxicity and poor crop establishment (Miller et al., 1971).

Foliar sprays are also an effective method of fertilizer application but this method is not suitable for supplying B to early plant growth stages (e.g. just after establishment) and also requires a separate fertilizer application in addition to application of macronutrients. Foliar application rates usually are about 50% lower than soil application rates (Mortvedt and Woodruff, 1993).

Granular or fluid nitrogen (N), phosphorus (P) and potassium (K) fertilizers are often used as carriers of B, with B incorporated into the macronutrient fertilizer because it is difficult to apply such low rates of B sources to soil separately (Mortvedt, 1991). Boronated fertilizers may be produced during manufacturing to supply the recommended B rate for a crop when NPK fertilizers are applied at the recommended rate (Mortvedt and Woodruff, 1993). For example, a 10-10-10 fertilizer containing 0.25% B would provide 1 kg B/ha if the fertilizer was applied at a rate of 400 kg/ha (Mortvedt and Woodruff, 1993). Soluble B sources may be easily applied with most fluid NPK fertilizers to provide the recommended B rates for crops (Mortvedt and Woodruff, 1993).

Boron can also be applied by bulk blending granular fertilizer borate with granular NPK sources (Mortvedt and Woodruff, 1993). The main advantage of this method is the flexibility of producing fertilizer grades which will provide the recommended rates of B as well as N, P and K for a given field (Mortvedt and Woodruff, 1993). The main disadvantage of applying B with bulk-blended fertilizers is that segregation of the B source from the other fertilizer

components during blending and subsequent handling is possible (Mortvedt and Cox, 1985). Most B sources are crystalline; therefore, their average particle size is much smaller than that of granular NPK fertilizers (Gupta, 1993b). As such, these B sources will easily segregate from the granular macronutrient fertilizer (Mortvedt and Woodruff, 1993). Segregation interferes with the uniform application of B in the field, which is critical because of the low B application rate and the possibility of toxicity due to “patchy” over-application (Mortvedt and Woodruff, 1993).

### 2.4.3 Granulation of boron fertilizer

Applying pure B fertilizer to soil separately is often not cost-effective. Bulk blending of B with other micronutrients is also an unattractive option, as it results in poor nutrient distribution in the field (Figure 4). Granulation of micronutrients with macronutrient fertilizers may allow for a single fertilizer application and a more even nutrient distribution. The efficiency of B fertilization could be increased if the B is co-granulated with other macronutrients such as mono-ammonium phosphate (MAP) and/or diammonium phosphate (DAP) to ensure an even nutrient distribution.

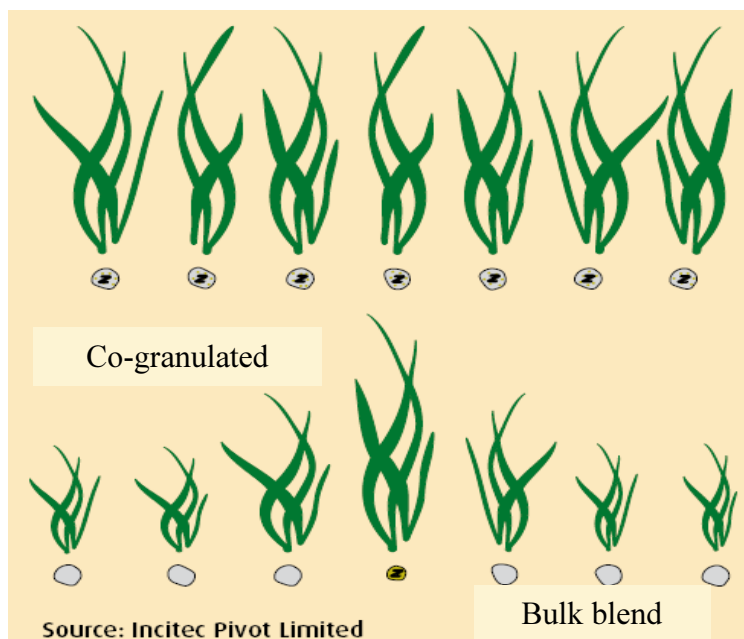


Figure 4 Distribution effects of micronutrient fertilizers (Incitec Pivot Ltd).

Granulation is a process of particle enlargement or agglomeration and is accomplished by the formation of inter-particle bonds between primary particles to form new entities called granules (Liu, 2002; Sherrington, 1968). Granulation processes are used extensively on powdered materials within pharmaceutical, food and agricultural industries to improve flow properties, strength, product appearance, shape and structural form (Mangwandi et al., 2012). Granulation can be used to solve different powder-flow problems, to ensure better results when mixing difficult powders, to reduce dust hazard problems, and to obtain controlled release of nutrients in fertilizers (Walker, 2007). The process seeks to produce nutrient homogeneity within and between granules.

Granulation is a key process in the fertilizer industry (Adetayo et al., 1993). The rolling drum is the simplest continuous granulation device, and is widely used in the granulation of fertilizer (Walker, 2007). The early application of this technology in the fertilizer industry was in the production of granular superphosphate fertilizer in 1935 and of mixed NPK fertilizers later on (Walker, 2007). With regard to B fertilizers, information on the incorporation and granulation of B with macronutrient fertilizers is limited.

#### **2.4.4 Boron fertilizer sources**

The most commonly used B fertilizer sources for correcting B deficiencies are sodium borates (Byers et al., 2001; Saleem et al., 2011). Fertilizer borate is the generic name given to  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$ , which contains 14.3 to 14.9% B (Table 4) (Mortvedt and Woodruff, 1993). It is produced by refining borax ores from old lake deposits (Mortvedt and Woodruff, 1993). Anhydrous borax (21.5% B) also is sold as a fertilizer, but it is not as commonly used as the pentahydrate product (Mortvedt and Woodruff, 1993).

Another B fertilizer used mainly as a foliar spray is Solubor, which is further refined from borax (Gupta, 1993b). Its solubility is higher than that of fertilizer borate, so it is easier to



dissolve in water for foliar sprays (Mortvedt and Woodruff, 1993). Solubor is a specially prepared spray-dried product in a very fine powder form with an approximate formula of  $\text{Na}_2\text{B}_8\text{O}_{13}\cdot 4\text{H}_2\text{O}$ , containing 20.5% B (Table 4) (Mortvedt and Woodruff, 1993).

Boric acid is produced by reacting refined fertilizer borate with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (Mortvedt and Woodruff, 1993). This product also is highly water soluble, but it is more costly per unit of B; therefore, it is not commonly used as a source of fertilizer B (Mortvedt and Woodruff, 1993). Colemanite and ulexite have been used as slow-release B sources (Hortenstine et al., 1958). These products are refined from ores and their availability in soil is highly dependent on the mineral particle size (Hortenstine et al., 1958).

Another B source is fritted glass which contains variable B concentrations (Table 4) (Gupta, 1993b). The frits are produced by mixing powdered borates with a silicate matrix which is melted in a furnace, quenched, dried and milled (Roberts, 1976). Solubility of B in these products is controlled mainly by their particle size (Roberts, 1976). The frits must be finely divided to be effective for plant uptake (Gupta, 1993b). However, they are difficult to apply with other granular fertilizers to soil because of segregation due to significant differences in particle size (Gupta, 1993b). Because of their low water solubility, B frits are applied to sandy soils in high rainfall areas where leaching is a problem (Mortvedt, 1968). However, frits are more appropriate for maintenance programs than for correcting severe B deficiencies (Mortvedt and Woodruff, 1993).

Table 4 Boron compounds commonly used as fertilizers.

<b>Boron source</b>	<b>Chemical formula</b>	<b>Solubility in water</b>	<b>% Boron</b>
Solubor	$\text{Na}_2\text{B}_8\text{O}_{13}\cdot 4\text{H}_2\text{O}$	Very soluble	20.5
Borax	$\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$	Soluble	11.3
Fertilizer borate	$\text{Na}_2\text{B}_4\text{O}_7\cdot 5\text{H}_2\text{O}$	Soluble	14.3 – 14.9
Anhydrous borax	$\text{Na}_2\text{B}_4\text{O}_7$	Soluble	21.5
Boric acid	$\text{H}_3\text{BO}_3$	Soluble	17.5
Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11}\cdot 5\text{H}_2\text{O}$	Moderately soluble	15.8
Ulexite	$\text{NaCaB}_5\text{O}_9\cdot 8\text{H}_2\text{O}$	Moderately soluble	13.3
Boron frits†	-	Slightly soluble	2 - 11

Adapted from Mortvedt and Woodruff (1993). † fused borate and silica matrix

Experimental studies have demonstrated that the danger of B toxicity can be reduced by the use of slowly soluble B materials either in mineral forms such as colemanite (Page and Cooper, 1955) or glass frits (Holden and Hill, 1958). The amount of B that can be safely applied to a soil may be approximately doubled with colemanite.

Soluble sources usually have little residual effect (Mortvedt and Woodruff, 1993). The length of residual effect of B fertilizer was reported to be markedly influenced by the method of application and dissolution rate of the fertilizer, with slow-release sources having more residual effect (Wilson et al., 1951). However, Shorrocks (1997) pointed out that it is not possible to specify the length of residual effect and made recommendations until precise local experiments have been conducted.

## **2.5 Slow-Release Boron Fertilizers**

### **2.5.1 Need for slow-release boron fertilizers**

Boron leaching in high rainfall areas may reduce the amount of available B to crops. Following periods of heavy rainfall, highly soluble sodium borates are likely to be leached from the root zone and therefore fail to supply the crop with the necessary B. On the other hand, toxic concentrations for seedlings may occur shortly after application when using

soluble sodium borates (Page and Cooper, 1955). To counter the possibility of leaching in high rainfall areas, slowly soluble B sources are needed to provide a prolonged B release rate (Byers et al., 2001).

### **2.5.2 Advantages of slow-release fertilizers for crop production**

Slow-release fertilizers are fertilizers containing plant nutrient(s) in a form which delays its availability for plant uptake and use after application (Trenkel, 1997). As the nutrient(s) is taken up by the plants, additional nutrient(s) dissolve to maintain dissolved nutrient(s) in solution at about the same concentration; and if the soil water content decreases because of evapotranspiration, the nutrient(s) concentration in solution decreases because of precipitation (Michaud, 1982). Slow-release fertilizer reduces the risk of burning in the plants by over-fertilization or of losing fertilizer by water run-off or by leaching under high rainfall or heavy irrigation, since only a small controlled amount of fertilizer is soluble in water at any particular time (Mortvedt, 1994).

Slow-release fertilizers can meet the crop nutrient demand for the entire season through a single application, thus saving spreading costs and time (Shaviv, 2000). Because of the slow release characteristic and slow solubility of the nutrient in the fertilizer composition, the fertilizer can be applied safely at planting, prior to the plant's requirement at a different growth stage (Oertli and Lunt, 1962). Moreover, slow-release fertilizers can reduce the demand for short-season manual labour which is, for instance required during critical periods in rice paddies (Gandeza et al., 1991).

### **2.5.3 Types of slow-release boron fertilizers**

In general, two types of slow-release fertilizers can be distinguished: (i) coated products, in which the coating provides a physical barrier that slows the release from the nutrient in the granule, and (ii) products with inherent low solubility of the nutrient of interest.

Slow-release B fertilizers could be created by coating soluble B compounds (pure or co-granulated with macronutrient fertilizer) to slow down the release of B. The rate of release can be controlled by varying the chemical composition, thickness or porosity of the coating. Some of the coating materials that have been used previously for slow-release macronutrient fertilizers are polymers such as polyacrylamide, polyethylene, polystyrene, polyurethane, acrylic resins, epoxy polyester and polyvinyl chloride (Sharma, 1979). Elemental sulfur (S), a low-cost secondary plant nutrient, was also found to be suitable for coating fertilizer, due to its ability to melt at about 156°C, thus enabling spraying molten S onto granular urea and possibly onto other fertilizers as well (Shaviv, 2005). There has been much research carried out on coating macronutrient fertilizers, especially N, P and K fertilizers with polymers and S and there are several commercially available products (Bandyopadhyay et al., 2008; Christianson, 1988; Hassan et al., 1992; Jarrel and Boersma, 1979; Jarrel and Boersma, 1980; Oertli and Lunt, 1962; Trenkel, 1997). To my knowledge, using polymer or S coatings to create a slow-release B fertilizer has not been investigated.

Studies have been conducted to assess the use of sparingly soluble B minerals or compounds as slow-release B fertilizers. Glass frits which contain B have been used as a slow-release source for B (Holden et al., 1962). However, they are difficult to apply with other granular fertilizers to soil because of segregation due to differences in particle size (Mortvedt and Woodruff, 1993). Another disadvantage of glass frits is their production process which involves very high temperatures, corrosive melts and energy costs (Roberts, 1976).

Minerals such as colemanite and ulexite also have been evaluated as slow-release B sources (Eaton, 1932). Colemanite, while affording initial protection to seedlings, has been reported to form lime *in situ* in soil and to adversely affect the availability of other essential nutrients needed by plants (Gupta, 1993b). In another study, incorporation of colemanite or sodium borate with NPK fertilizers resulted in similar yields of cotton and sunflower (Rowell and

Grant, 1975). The solubility and dissolution rate of colemanite and ulexite are highly dependent on their particle size (Byers et al., 2001) and the proportion of Na, Mg and Ca present in the materials (Mortvedt, 1994), and hence, depending on how they are used, these sources may not act as slow-release B fertilizers. In addition, both colemanite and ulexite contain naturally occurring impurities such as arsenic (As) that can limit their use (Cook, 2010). Therefore, other B minerals or compounds with slow-release formulations are still required.

Boron phosphate ( $BPO_4$ ), a mineral with low solubility is expected to provide a slow-release form of B not readily leached by rainfall (Ray, 1972). When  $BPO_4$  is incorporated into soil, it slowly releases soluble B over a period of time corresponding at least to the critical uptake period of the crop (Magda et al., 2010). Boron phosphate has not been tested yet for use as co-granulated fertilizer sources for B and the factors controlling the release of B from  $BPO_4$  in soil are not well known and require further study.

## **2.6 Summary**

Boron is an important nutrient for normal plant growth and development; B deficiency and toxicity problems affect crop production worldwide. Boron deficiency usually occurs in coarse-textured soils in high rainfall regions, whilst toxicity is attributed to high B application rates and from irrigation water containing B. The most commonly used B fertilizer source is water soluble sodium borate (borax), which is vulnerable to leaching losses and poses a risk of B toxicity to seedlings.

Less soluble B sources such as colemanite, ulexite and B frits show promise as slow-release B fertilizers. The possibility of using  $BPO_4$  as a B source for plant growth also has been reported. However, we have little knowledge regarding the B release kinetics from this material or its compatibility with macronutrient fertilizers.

There is a significant need for the supply of economically viable slow-release B fertilizers to improve B nutrition in agricultural crops. Therefore, I developed a series of experiments to formulate and synthesize  $BPO_4$  compounds; and examine their characteristics. Boron phosphate compounds were chosen as the main materials because the solubility can be modified by changing the temperature and heating times. Several commercially available B sources, namely borax, ulexite and colemanite, were also included in this study for comparison.

## **2.7 Aims and Objectives**

The aim of this study was to develop novel slow-release B fertilizers for improving fertilizer use efficiency in term of nutrient uptake and crop yield especially in high rainfall regions.

The specific objectives of this study were to:

- i. formulate, synthesize and characterize  $BPO_4$  compounds as raw materials to produce slow-release B fertilizer sources;
- ii. develop a co-granulated fertilizer of macronutrients with B so that the B is not easily leached out;
- iii. develop a co-granulated fertilizer of macronutrients with B that is relatively inexpensive and safe to seedlings, and assess the seedling toxicity of this fertilizer;
- iv. assess the effect of the co-granulated slow-release B fertilizer sources on plant uptake under simulated leaching conditions; and
- v. assess the residual effect of the co-granulated slow-release B fertilizer sources for a subsequent crop.

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**Formulation, synthesis and characterization of boron phosphate (BPO<sub>4</sub>) as raw materials to develop slow-release boron fertilizers**

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**Chapter 4**

**Slow-release boron fertilizers: co-granulation of boron sources with mono-ammonium phosphate (MAP)**

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Chapter 4 was written in manuscript style and submitted to Soil Research

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Slow-release boron fertilizers: co-granulation of boron sources with mono-ammonium phosphate (MAP)

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**Slow-release boron fertilizers: co-granulation of boron sources with mono-ammonium phosphate (MAP)**

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## Abstract

The application of pure boron (B) fertilizers, independent of other macronutrients, is impractical due to the increased cost of dual handling and spreading. Bulk blending of B with other micronutrients is also an unattractive option as the relatively low rates of B required results in poor nutrient distribution in the field. Co-granulating B with other macronutrients such as mono-ammonium phosphate (MAP) may overcome these problems. Five B sources (boron phosphate (BPO<sub>4</sub>) synthesized at 500 and 800 °C for 1 h, colemanite, ulexite and borax) were co-granulated with MAP to targeted B contents of 0.5, 1.0 and 2.0%. The co-granulated BPO<sub>4</sub> had lower water solubility than co-granulated colemanite, ulexite and borax. Boron released from co-granulated borax, ulexite and colemanite was remarkably greater than co-granulated BPO<sub>4</sub> products. Over a 4-week soil incubation period with weekly leaching of one pore volume of water, the cumulative B release from co-granulated ulexite, borax and colemanite was 97, 75 and 58%, respectively, but only 16 and 4% for the co-granulated BPO<sub>4</sub> synthesized at 500 and 800 °C, respectively. Co-granulated BPO<sub>4</sub> products have potential as a high quality fertilizer to increase crop yield with slow B release.

**Keywords:** boron phosphate, dissolution, leaching, nutrient release

#### 4.1 Introduction

Boron (B) is one of the essential micronutrients required for normal plant growth and cell development (Gupta 1979). Deficiencies as well as toxicities of B result in many anatomical and physiological changes in plants (Berger 1949). For the past 30 years, research on plant B nutrition has progressed significantly and the application of B fertilizer has become a standard practice in many B deficient regions. Boron fertilizers in the form of very soluble B compounds such as sodium borate or borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ) and less soluble B sources such as colemanite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ) and ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ) have been added to soil to maintain plant growth (Wear and Wilson 1954).

In any farming system, fertilization represents one of the most important items contributing to farm costs (Tissot *et al.* 1999). Separate application of pure B fertilizer is not cost-effective. Bulk blending of B with other micronutrients is also an unattractive option, as it results in poor nutrient distribution in the field. Granulation of micronutrients with macronutrient fertilizer allows for a single fertilizer application and a more even micronutrient distribution.

Granulation is a process of particle enlargement or agglomeration and is accomplished by the formation of inter-particle bonds between primary particles to form new entities called granules (Liu 2002; Sherrington 1968). Granulation processes are used extensively on powdered materials within pharmaceutical, food and agricultural industries to improve flow properties, strength, product appearance, shape and structural form (Mangwandi *et al.* 2012). Granulation can be used to solve different powder-flow problems, to ensure better results when mixing difficult powders, to reduce dust hazard problems, and to obtain controlled release of nutrients in fertilizers (Walker 2007).

Boron is only required by plants in small amounts, with recommended fertilization rates ranging from 0.25 to 3.0 kg B/ha, depending on crop requirement and method of application (Mortvedt and Woodruff 1993). With the low B application rates and the use of soluble B sources, B fertilization has always been a problem, especially in high rainfall areas. Water soluble B fertilizers can provide high B concentrations in soil solution after application to soil, which can be hazardous to crop seedlings, while rapid leaching of B from the soil may result in an inadequate supply of B for plant uptake later in the growing season in high rainfall areas (Shorrocks 1997). Therefore, fertilizer sources with low water solubility and slow B release are necessary for the effective management of B fertilization in humid regions. Slow-release fertilizers can meet the crop nutrient demand for the entire growth stage through a single application, thus saving spreading costs and time (Shaviv 2000). These slow-release fertilizers can be applied safely at planting, because of their slow-release characteristics. Up to now, research and development on B fertilizers, particularly on the co-granulation of slow-release B sources with other macronutrients, has received very little attention.

One of the B sources that has potential to be used as a raw material for slow-release B fertilizer is boron phosphate ( $BPO_4$ ). The considerably high B content (10% by weight) in  $BPO_4$  and its low solubility make this compound an efficient slow-release B fertilizer source (Magda *et al.* 2010). Magda *et al.* (2010) reported the formation of  $BPO_4$  by neutralizing phosphoric acid ( $H_3PO_4$ ) with ammonia ( $NH_3$ ) solution with the addition of sodium tetraborate pentahydrate ( $Na_2B_4O_7 \cdot 5H_2O$ ) and calcining above 500 °C. However, this material has not been tested for use as a slow-release B source for co-granulation with other macronutrients in compound fertilizers.

We attempted here to formulate slow-release B fertilizers by co-granulating  $BPO_4$  compounds with the commonly used macronutrient mono-ammonium phosphate (MAP).

Boron phosphate compounds synthesized at 500 and 800 °C for 1 h were selected for the co-granulation process with MAP. These two BPO<sub>4</sub> compounds were characteristically suitable and have potential to be used as raw materials for slow release B sources (Abat *et al.*, Chapter 3). Three other commercially available B sources borax, ulexite and colemanite were also co-granulated with MAP. All of the co-granulated products were tested for their suitability as a slow-release B fertilizer.

## **4.2 Materials and Methods**

### **4.2.1 Boron sources used in the co-granulation process**

Five B sources were used as raw materials in the co-granulation process; two BPO<sub>4</sub> compounds, colemanite, ulexite and borax. The BPO<sub>4</sub> compounds were synthesized by mixing boric acid (H<sub>3</sub>BO<sub>3</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and heating the mixture at 500 or 800 °C for 1 h (Abat *et al.*, Chapter 3). The procedure has been modified based on the method by Becher (1963). The acids used were analytical reagent (AR) grade (99.8% min) H<sub>3</sub>BO<sub>3</sub> (Merck) and concentrated H<sub>3</sub>PO<sub>4</sub> (85% w/w, Acros Organic). The other three B sources were the commercially available colemanite (Active Micronutrient Fertilizers), ulexite (ChemSupply) and di-sodium tetraborate (borax) (BDH Analar).

### **4.2.2 Co-granulation of B sources with MAP**

The equipment set up for the co-granulation process consisted of a stainless steel pan granulator, Masterflex air pump, peristaltic pump, Bosch heat gun and spray nebulizer (Figure 1). The optimum conditions for the co-granulation process were as follows: Masterflex air pump speed set at 8.6 mL/s, nebulizer spray rate at 0.12 mL/min, Bosch heat gun set at 500 °C and granulation speed at 1.0 rotation per min. Lignosulfonate (Lignobond DD from Lignotech, South Africa) was used as a binder. The quantities of B sources and MAP to obtain pre-determined B contents of 0.5%, 1% and 2% were thoroughly mixed and ground (< 250 µm) together using a grinder. The ground mixture (~20 g) was then transferred

into a stainless steel laboratory scale pan granulator. The binder solution was prepared by dissolving 1.03 g of lignosulfonate in 100 mL of deionized (DI) water and pumped using the peristaltic pump to the nebulizer at ambient temperature. The nebulizer, delivering an atomized spray, was positioned at an angle such that the binder was directed toward the tumbling materials rather than onto the pan surface while the pan granulator was rotating. The binder spray rate was adjusted depending on the moisture content of the mixture. A heat gun, set at a distance from the drum, was used to slowly and evenly dry the granules. This slow drying avoided localized over-heating and abrasion of granules and instead produced hard granules with lower porosity. The materials were rotated for about 15 to 20 min. Fines ( $\leq 1$  mm) were reground and fed back into the drum, after which the granules produced were poured into a container and dried overnight in an oven at 40 °C. The granules then were sorted using a series of mesh size sieves. The granules were kept in an airtight container prior to analysis.

#### **4.2.3 pH determination of the co-granulated products**

One gram of each sample was weighed into a centrifuge tube and 10 mL of DI water was added. The mixture was shaken in an end-over-end shaker for 1 h. The solution was left standing for 30 min and then the pH was measured. Duplicate measurements were made.

#### **4.2.4 Total elemental analysis of co-granulated products in *aqua regia* mixture**

Total elemental analysis of the co-granulated products was performed by digesting about 0.1 g of each in an *aqua regia* (3 HCl: 1 HNO<sub>3</sub>) mixture. The solution then was analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). All samples were analyzed in triplicate.

#### **4.2.5 Determination of water soluble B and phosphorus (P) in the co-granulated products**

About 200 mg of each co-granulated product was weighed into a tube. Twenty mL of DI water was added into the tube and equilibrated by shaking on an end-over-end shaker for 24

h. The suspension then centrifuged for 30 min at 3500 relative centrifugal force (RCF). Five mL of supernatant was taken out from the suspension, filtered (0.45  $\mu\text{m}$  Sartorius filter) and kept for determination of B and P by ICP-OES. All samples were analyzed in duplicate.

#### **4.2.6 Dissolution of B from co-granulated B sources using a column perfusion technique**

The kinetics of B release from the co-granulated B fertilizers at 1.0% B content was determined using a column perfusion technique. The column was packed with acid washed sand (Sigma Aldrich). Glass wool was placed at the bottom of the column to obtain an even distribution of leaching solution and to prevent sand loss during leaching. Twenty grams of acid-washed sand was packed into the column. One gram of co-granulated B source was wrapped in a 0.5-mm mesh size cloth and placed on the surface of the sand and then covered with another 10 g of acid-washed sand. Glass wool was placed on the sand to minimize surface disturbance during leaching and to obtain an equal distribution of leaching solution to the whole surface. A 10 mM calcium chloride ( $\text{CaCl}_2$ ) was used as the leaching solution and pumped at a flow rate of 2 mL/h using a peristaltic pump from the bottom of the sand column. The leachate was collected at 5-hour intervals. The remaining B material and sand above the fertilizer (top 10 g sand) were removed carefully from the column at the end of the dissolution process, air-dried and digested to check the mass balance for B. The concentrations of B and P in the leachate and digests were measured by ICP-OES. All samples were run in duplicate.

#### **4.2.7 Boron release from the co-granulated products in soil column study**

The kinetics of B release from the co-granulated products with 1.0% B content was also determined in a soil column study. Granular MAP was included as a control (no B) treatment. A column without any fertilizer was also included.

Sixty grams of Mt Compass soil was packed into a leaching column (60 ml Removable Luer Lock syringe; internal diameter = 3 cm, height = 11 cm) to an approximate bulk density of

1.2 g/cm<sup>3</sup> and height of 7 cm. Mt Compass is a coarse-textured soil and has low concentrations of available (hot-water extractable) B (Table 1). The base of the column was covered with a thin layer of glass wool and a thin layer (0.5 cm) of acid-washed sand. Soil was added to the column to a height of 6 cm. Eight granules of co-granulated B fertilizers (corresponding to about 0.2 g fertilizer; 2 mg B) were wrapped in a mesh cloth (0.5 mm mesh size) and placed on the soil and covered with about 1 cm of soil. All treatments were replicated three times.

The column was saturated by slowly pumping DI water from the bottom of the column using a peristaltic pump set to a flow rate of 10 mL/h until the soil was saturated. The column was brought to field capacity by applying vacuum through a 25 cm<sup>3</sup> syringe, drawn to the 12 cm<sup>3</sup> marks, after allowing for gravity drainage for about 30 min. The top of the column was covered with glass beads to minimize moisture loss, weighed and left to stand at room temperature.

The moisture content was maintained at field capacity, correcting for column weight change on a weekly basis. The columns were leached with ~ one pore volume (21.25 mL) of DI water every week for four weeks. A vacuum suction was applied using 25 cm<sup>3</sup> syringes to extract the solution from the column. The volume of the leachate was recorded and filtered through a 0.45 µm Sartorius hydrophilic syringe filter. The pH of the leachate was measured after every leaching. The leachate was acidified with 10 µL of concentrated HNO<sub>3</sub> and stored at 4 °C prior to analysis. After four weeks, the fertilizer granules were recovered from the soil column by carefully removing the soil around the mesh cloth. The recovered granules were digested in *aqua regia* mixture. The soil below the granules was collected and mixed homogeneously. A subsample was digested in *aqua regia* and the B concentration in the digests was analyzed using ICP-OES.



## **4.3 Results**

### **4.3.1 Physical appearance of the co-granulated products and granule size**

The granules produced were spherical in shape and regular in size. The standard required specification for fertilizer granules is that at least 85% of the granules have sizes between 1.0 and 4.0 mm (Rico *et al.* 1995). About 90 to 95% of the granules obtained from the various co-granulated products were of the size range between 1.0 and 4.0 mm, with about 90 % between 2.35 and 3.35 mm. About 5% of the granules were less than 1.0 mm in mesh size. The fraction greater than 4.0 mm only accounted for about 1 – 2%.

### **4.3.2 pH of co-granulated products**

The solution pH of the MAP without added B was 4.3. The solution pH of the MAP fertilizer co-granulated with  $\text{BPO}_4$  ranged from pH 4.2 to 4.4. For the fertilizers co-granulated with colemanite, ulexite and borax, which have a basic reaction, the solution pH was between 5.0 and 5.5.

### **4.3.3 Total B and P in the co-granulated products**

The B concentrations obtained in most of the co-granulated products were close to the target B contents ( $\leq 10\%$  difference from target). The P concentrations in the co-granulated products ranged from 20 to 24% (data not shown).

### **4.3.4 Water soluble B in the co-granulated products**

For the co-granulated ulexite and borax products,  $>90\%$  of B was water-soluble (Table 2). For co-granulated colemanite, the B solubility ranged from 74 to 81% of the total B content (Table 2). The solubility of B in the co-granulated products containing  $\text{BPO}_4$  synthesized at 500 °C was between 16 and 26% of the total B content. The solubility of B in co-granulated  $\text{BPO}_4$  synthesized at 800 °C was only about 6% of the total B, irrespective of the total B content (Table 2).

#### **4.3.5 Kinetics of B release in column perfusion technique**

The dissolution of B from the co-granulated ulexite and borax was rapid and B was almost completely leached out after about 48 h (Figure 2A). For co-granulated colemanite, 95% of total B was released after about 72 h. Boron release after 600 h of column dissolution was about 17% for the co-granulated BPO<sub>4</sub> synthesized at 500 °C and about 7% for that synthesized at 800 °C (Figure 2A). The concentration of B in the leachates of co-granulated ulexite, borax and colemanite were high at the beginning (137, 189 and 89 mg B/L, respectively), and strongly decreased over time until the concentration was almost below detection limit (~10 µg/L) (Figure 2B). The B concentrations in the leachate of the co-granulated BPO<sub>4</sub> products gradually decreased until they reached a near constant value (Figure 2B).

#### **4.3.6 Soil column study**

The pH of the leachate from the first leaching ranged from 5.19 to 5.56 (Figure 3). The pH of the leachate then gradually increased to about 6.10 and 6.50 after two leaching events (Figure 3). The changes in the pH were mainly determined by the MAP fertilizer addition. The majority of added P was rapidly leached out because of the low P retention of the soil.

The B released from the soil followed a similar trend as observed in the sand column study. Boron release from co-granulated ulexite was the fastest, with about 97% of added B leached over the four weeks (Figure 4A). This was followed by co-granulated borax (75% B leached) and co-granulated colemanite (58% B leached). For co-granulated BPO<sub>4</sub> synthesized at 500 °C, 16% of added B was leached after four weeks, while only 4% was released from the co-granulated BPO<sub>4</sub> synthesized at 800 °C (Figure 4A). The initial concentration of B in the leachates was high for co-granulated ulexite, borax and colemanite and much lower for the co-granulated BPO<sub>4</sub> products (Figure 4B).

Only about 2 to 3% of added B was recovered at the end of experiment in the residual granules of co-granulated ulexite, borax and colemanite (Table 3). A substantial amount of B was retained in the soil treated with co-granulated borax (10%) and co-granulated colemanite (33%). For the granules containing BPO<sub>4</sub>, 41% of B was recovered in the granules of co-granulated BPO<sub>4</sub> synthesized at 500 °C for 1 h and 31% of B was recovered from the soil. For the granules of co-granulated BPO<sub>4</sub> synthesized at 800 °C for 1 h, 44% of B was recovered in the granules and 38% in the soil (Table 3).

#### 4.4 Discussion

In a previous study, we determined the kinetics of B release from pure ulexite, borax, colemanite and BPO<sub>4</sub> compounds synthesized at 500 and 800 °C for 1 h using the same column dissolution technique (Abat *et al.*, Chapter 3). As a pure compound, the kinetics of B released from BPO<sub>4</sub> compound synthesized at 500 °C for 1 h was rapid and almost similar to those of pure ulexite and borax. Boron released from pure colemanite was slow. Thus, the kinetics of B released from these pure B sources in decreasing order was BPO<sub>4</sub> 500 °C ~ ulexite ~ borax > colemanite ~ BPO<sub>4</sub> 800 °C. This contrasts with the order of solubility found for the B sources co-granulated with MAP, which is: ulexite ~ borax > colemanite > BPO<sub>4</sub> 500 °C > BPO<sub>4</sub> 800 °C.

The differences between the pure B sources and co-granulated products can be explained by the conditions imposed by the MAP carrier. As a pure source, colemanite has high pH and low solubility. However, when co-granulated with MAP, the lower pH and the high P concentrations, which reduce the Ca<sup>2+</sup> concentration through Ca-P precipitation, increased the solubility of colemanite (Abat *et al.*, Chapter 3). This limits the use of these minerals (colemanite and ulexite) to produce slow-release B formulations with fertilizers such as single superphosphate (SSP), triple superphosphate (TSP) or MAP. This limitation does not apply to the BPO<sub>4</sub> compounds.

The concentration of B released from co-granulated  $BPO_4$  products in the soil column experiment was below the toxicity level of 5 mg B/L for most crops (Nable *et al.* 1997). These results indicate the potential of co-granulated  $BPO_4$  products as seedling-safe slow-release B fertilizer sources. The recovery results indicate that a significant amount of the B was retained in the soil (Table 3). The one week period between each leaching would have contributed to fixation of B by the soil. The initial concentration of B released from co-granulated  $BPO_4$  products is lower; therefore, B does not ‘flush’ through the soil and has time to be retained. With the more soluble B sources, the high B concentration at the beginning and the low pH would result in negligible B retention.

Several studies have pointed to fixation of B in soil. Eguchi and Yamada (1997) conducted a long-term field experiment (3 and 15 years) using slow-release B fertilizer on three soil types (diluvial, granitic and volcanic ash) in an area with an average precipitation of more than 2000 mm. After 15 years of cultivation, 40–60% of added B had leached from the topsoil and 10% was absorbed by plants. Of the 30-40% left in the topsoil, most B was present in a fixed form (Eguchi and Yamada 1997). Mortvedt (1968) carried out a study to determine the availability of B in borax incorporated with various macronutrient fertilizers with B contents ranging from 0.2 to 10%. The recovery of B from the soil treated with these products increased with the increasing concentrations of water soluble B in the products but decreased with time, indicating fixation of B in the soil (Mortvedt 1968). The fixation reactions of B prevent short term B leaching from the soil, but with time, this ‘fixed’ B may be desorbed back into the soil solution for plant uptake at a later stage.

Alternatively, the large percentages of B recovered in the soil for the  $BPO_4$  products are not due to fixation of B released from the granules, but due to particulate movement. As the leaching continued the granule would have disintegrated as P and N were released. The

fertilizer fine particles may have moved through the mesh cloth with the mass flow and hence have been recovered in the soil, rather than at the point of application.

#### **4.5 Conclusions**

Co-granulated products of MAP with  $BPO_4$  synthesized at 500 and 800 °C for 1 h show potential as slow-release B fertilizers. Boron release from the co-granulated  $BPO_4$  was slow and the initial B concentration around the granule is likely to be safe for most crop seedlings. Boron release from co-granulated ulexite, borax and colemanite was rapid with initial B concentration in fertilizer leachates exceeding the toxicity level for most crops. The application of slow release formulations will allow a relatively high B addition without inducing toxicity to plants immediately following application. Further research is underway to compare the toxicity effect of these co-granulated fertilizers on crop seedlings and to determine the availability of B to crops.

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## Figure captions

Figure 1. The equipment set up for the co-granulation process.

Figure 2. Dissolution kinetics of B release from co-granulated B sources using sand columns with 1 g product leached at 2 mL/h. Cumulative percentage of B leached from co-granulated B sources (A) and concentration of B released over time (B). The limit of detection (dotted line) is 10 µg/L.

Figure 3. pH of leachates in the soil column experiment.

Figure 4. Cumulative fertilizer B leached (A) and B concentrations in the leachates (B) of the co-granulated products in the soil column experiment. Error bars represent standard deviation (SD) of triplicates.



## Tables

Table 1 Physical and chemical properties of Mt Compass soil.

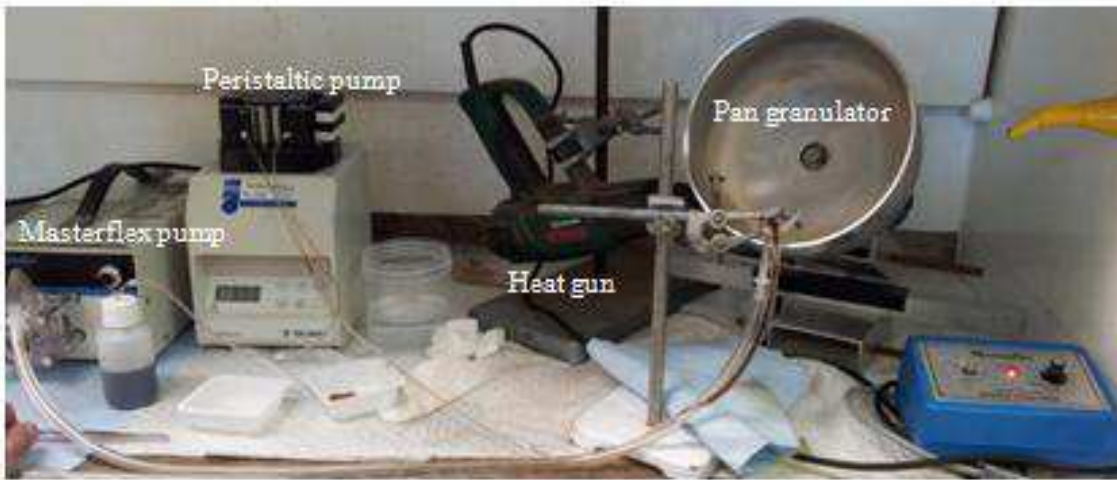
<b>Properties</b>	<b>Value/Concentration</b>
pH (CaCl <sub>2</sub> )	5.30
Conductivity (dS/m)	0.041
Phosphorus, P (mg/kg)	9.00
Potassium, K (mg/kg)	30
Sulphur, S (mg/kg)	3.70
Exchangeable calcium, Ca (cmol(+)/kg)	1.45
Exchangeable magnesium, Mg (cmol(+)/kg)	0.28
Exchangeable sodium, Na (cmol(+)/kg)	0.04
Exchangeable potassium, K (cmol(+)/kg)	0.03
Exchangeable aluminium, Al (cmol(+)/kg)	0.02
Hot water extractable boron, B (mg/kg)	0.20
Organic carbon (%)	0.54

Table 2 Percentage of water soluble B relative to total B in the fertilizer, for the different B sources that were co-granulated with MAP at a rate of 0.5, 1 or 2% B. Values in parentheses are standard deviation (SD) of two replicates.

<b>Product Name</b>	<b>Percentage water-soluble B (%)</b>		
	<b>0.5% B</b>	<b>1.0% B</b>	<b>2.0% B</b>
Co-granulated ulexite	104 (1)	99 (72)	106 (32)
Co-granulated borax	93 (31)	96 (52)	105 (12)
Co-granulated colemanite	81 (10)	77 (32)	74 (5)
Co-granulated BPO <sub>4</sub> 500 °C 1 h	16 (1)	21 (2)	26 (2)
Co-granulated BPO <sub>4</sub> 800 °C 1 h	6.5 (0.0)	5.4 (0.8)	5.3 (0.3)

Table 3 Mass balance for the soil column experiment: percentage B recovered in the leachates (four pore volumes in total), or in the granules or the soil at the end of the experiment.

<b>Product name</b>	<b>Cumulative B added leached (%)</b>	<b>Boron recovered from granules (%)</b>	<b>Boron recovered from soil (%)</b>	<b>Total (%)</b>
Co-granulated ulexite	97	1.9	0.12	99
Co-granulated borax	75	1.8	9.7	87
Co-granulated colemanite	58	2.9	33	94
Co-granulated BPO <sub>4</sub>	16	41	31	88
500 °C 1h				
Co-granulated BPO <sub>4</sub>	4.0	44	38	86
800 °C 1h				



**Figure 1**

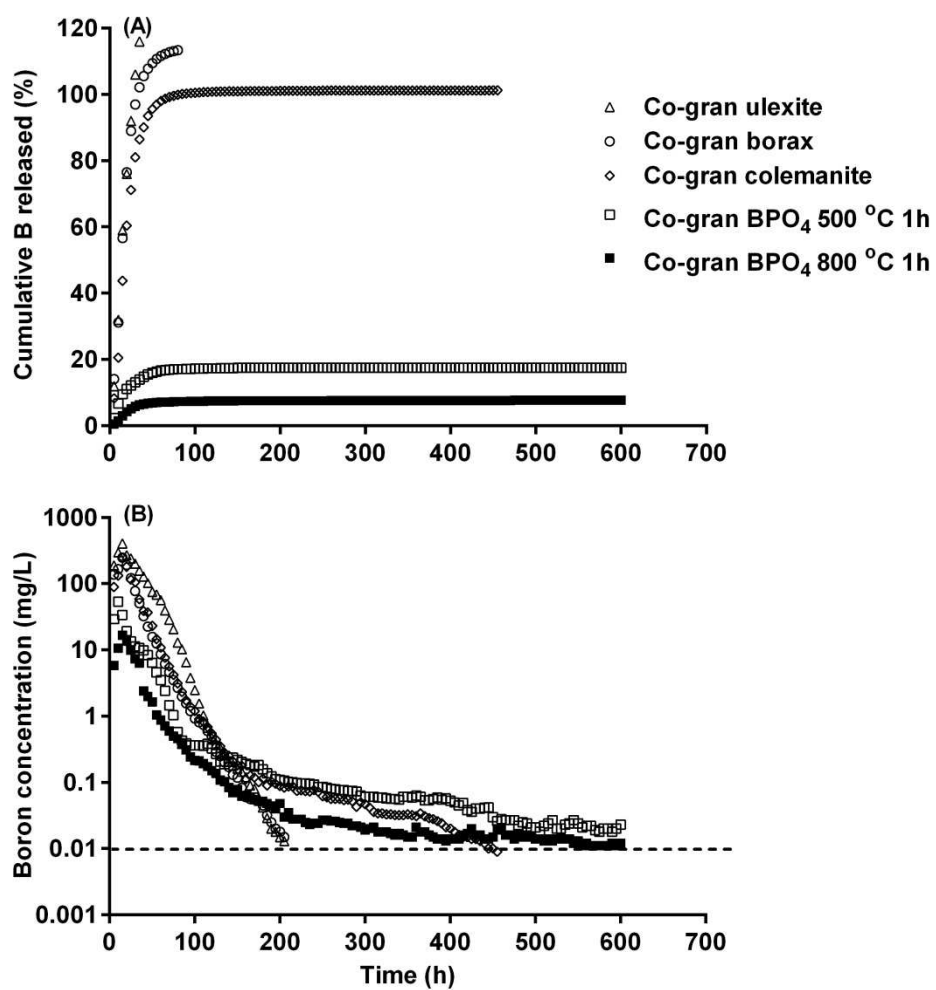


Figure 2

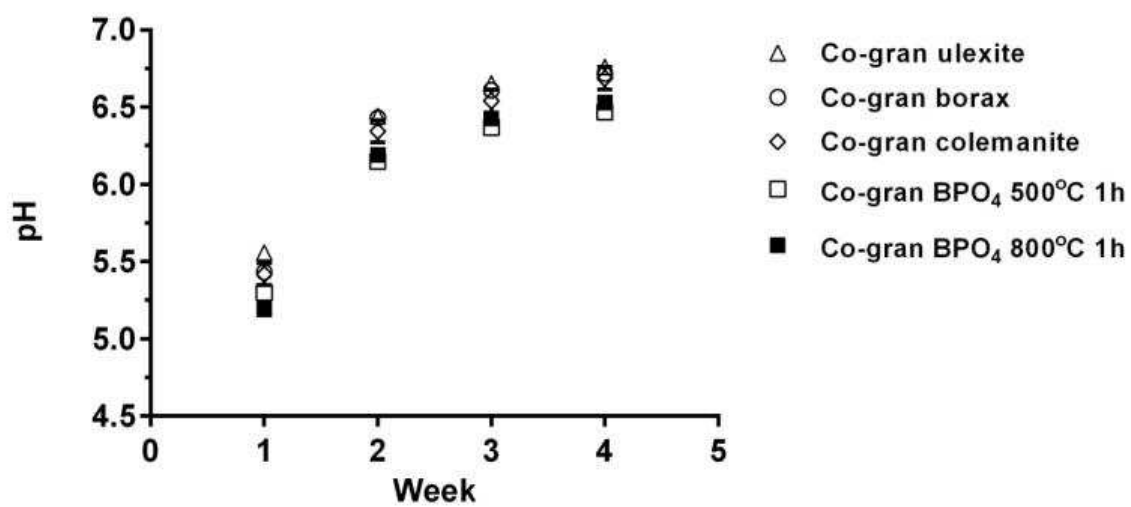


Figure 3

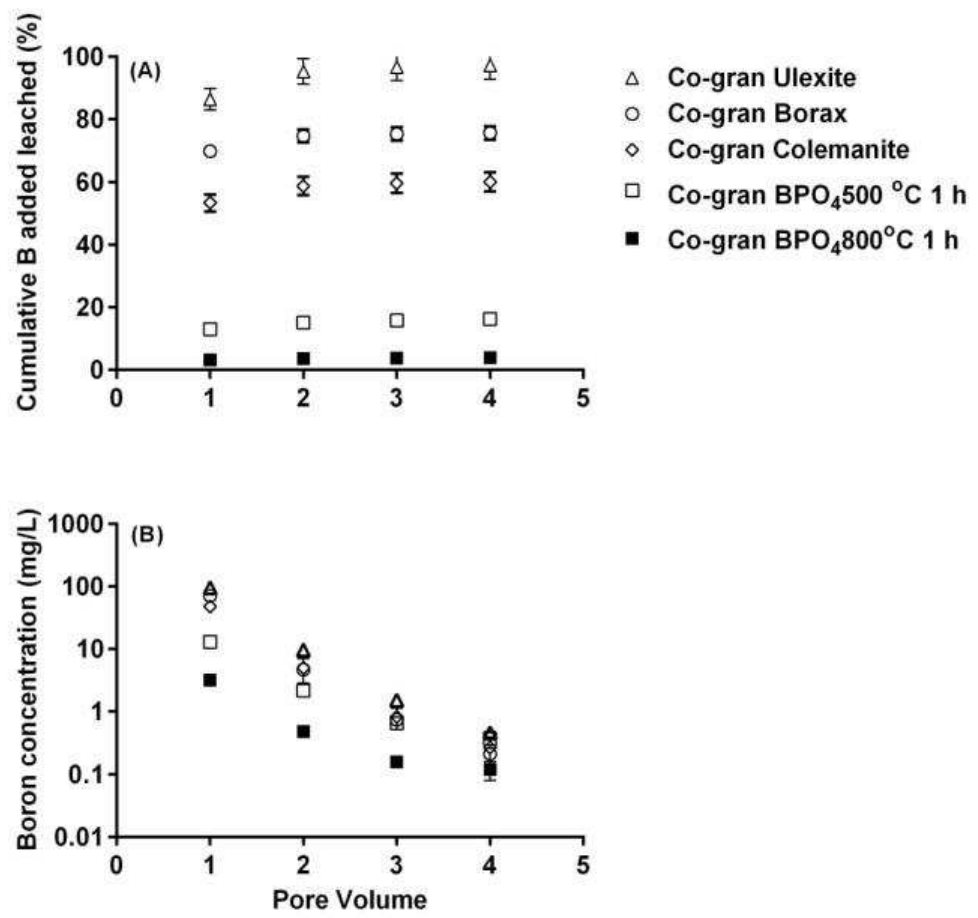


Figure 4

**Chapter 5**

**Boron phosphates (BPO<sub>4</sub>) as seedling-safe and slow-release boron fertilizer sources**

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Chapter 5 was written in manuscript style and submitted to Plant and Soil Journal



**STATEMENT OF AUTHORSHIP**

**Boron phosphate (BPO<sub>4</sub>) as seedling-safe and slow-release boron fertilizer sources**

Plant and Soil 2014; Submitted paper.

**Margaret Abat (Candidate)**

Designed and conducted all research experiments, analyzed and interpreted the data, drafted wrote the manuscript and acted as the corresponding author.

I hereby certify that the statement of authorship is accurate.

Signed: .....

Date: 1<sup>st</sup> December 2014

**Fien Degryse**

Contributed to the research ideas and design. Supervised the research work, helped with the data interpretation and provided critical evaluation of the manuscript.

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Date: 1<sup>st</sup> December 2014

**Roslyn Baird**

Contributed to the research ideas and design. Supervised the research work, helped with the data interpretation and provided critical evaluation of the manuscript.

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Date: 1<sup>st</sup> December 2014

**Michael J McLaughlin**

Contributed to the research ideas and design. Supervised the research work, helped with the data interpretation and provided critical evaluation of the manuscript.

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Date: 1<sup>st</sup> December 2014

## **Boron phosphates (BPO<sub>4</sub>) as seedling-safe boron fertilizer sources**

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## **Boron phosphates (BPO<sub>4</sub>) as seedling-safe boron fertilizer sources**

### **Abstract**

*Background and aims* Soluble boron (B) sources pose a risk of B toxicity to seedlings just after planting and leaching losses after application and before plant uptake. Boron phosphate (BPO<sub>4</sub>) has low water solubility and slowly releases B, and hence could be safe for seedlings. Therefore, we investigated the toxicity effect of several B sources co-granulated with mono-ammonium phosphate (MAP) on canola seedlings.

*Methods* Ulexite, borax, colemanite and BPO<sub>4</sub> compounds synthesized at 500 °C or 800 °C for 1 h were co-granulated with MAP at inclusion rates of 0.5, 1.0 and 2.0% B. The seedling toxicity of these products was evaluated by placing a fertilizer granule in the centre of a soil-filled Petri dish in which canola was seeded. The area of the non-vegetated zone around the granule application site was evaluated after seven and 12 days of growth.

*Results* Co-granulated ulexite, borax and colemanite showed toxicity symptoms at the lowest concentration of 0.5% B, and the area of the affected zone increased with increasing concentrations of B in the granule, whereas no toxicity symptoms were observed with the application of co-granulated BPO<sub>4</sub> products even at 2.0% B content. Hot water-soluble B concentrations were measured in concentric sections around the granule application site and were in agreement with the toxicity results, with concentration in the toxic range close to the granule for the most soluble B sources.

*Conclusions* Co-granulated BPO<sub>4</sub> products have potential as seedling-safe B fertilizer sources.

**Keywords:** boron phosphate, slow-release fertilizer, toxicity

## 5.1 Introduction

Boron (B) is an essential micronutrient required for normal plant growth and development (Gupta 1979). Deficiency and toxicity of B are widespread problems (Shorrocks 1997), and may limit the yield and reduce the quality of crops (Camacho-Cristobal et al. 2008; Marschner 1986). Many studies on B fertilization indicate that the concentration range between deficiency and toxicity is narrow and application of B can be extremely toxic to plants at concentrations only slightly above optimum levels (Gupta 1983; Keren and Bingham 1985).

The application of fertilizer to soil at the same time as seed planting has become an increasingly common approach to supply crop nutrients, as this gives newly emerged seedlings early access to nutrients (Qian and Schoenau 2010). This strategy was found to be effective for phosphorus (P) fertilizers due to the low mobility of P in the soil (Qian and Schoenau 2010). However, this technique may not be suitable with fertilizers that contain a soluble B source, as toxicity is likely to occur when fertilizer is banded with the seed (Miller et al. 1971).

Soluble B sources such as sodium borate or borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and boric acid ( $\text{H}_3\text{BO}_3$ ) are the most commonly used B fertilizer sources to maintain plant growth (Wear and Wilson 1954). However, not only do these soluble B sources pose a risk of B toxicity to seedlings just after planting, leaching losses after application and before plant uptake may result in low fertilizer use-efficiency in high rainfall areas (Mortvedt 1994). Slow-release B sources would reduce both the risk of seedling toxicity and of leaching losses. It has been suggested that colemanite ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ) and ulexite ( $\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$ ) may serve as slow-release B sources (Wear and Wilson 1954). Byers et al. (2001) found that B concentrations in alfalfa were lower with colemanite

than with granubor or ulexite as the B source. Broschat (2008) found that B release in sand columns followed the order: borax > ulexite > colemanite. However, we found that co-granulation of ulexite and colemanite with mono-ammonium phosphate (MAP) increases the solubility of these slow-release sources, thus counteracting their slow-release characteristics (Abat et al. 2014a) (unpublished data, 2014) and potentially making them toxic to seedlings in close contact to the fertilizer. In contrast with colemanite or ulexite, boron phosphate (BPO<sub>4</sub>) maintains its slow-release characteristics when co-granulated with phosphate fertilizers like MAP (unpublished data, 2014). The relatively high B content (10%) in BPO<sub>4</sub> and its low solubility should make it an efficient slow-release B fertilizer source (Magda et al. 2010; Ray 1972).

We therefore investigated the effects of co-granulated BPO<sub>4</sub> fertilizer formulations on canola applied at planting, using a newly developed seedling toxicity test. Ulexite, borax and colemanite co-granulated with MAP were also included in this study for comparison. The objective of this study was to determine the effect of MAP co-granulated with different B sources on emergence and early growth of canola seedlings. Canola (*Brassica napus* L.) was used as test species because of its high B requirement.

## **5.2 Materials and Methods**

### **5.2.1 Boron fertilizer sources**

The B fertilizers consisted of MAP co-granulated with different B sources at 0.5, 1.0 or 2.0% B (unpublished data, 2014). The co-granulated B sources were borax (BDH Analar), ulexite (ChemSupply), colemanite (Active Micronutrient Fertilizer) or BPO<sub>4</sub> compounds. The BPO<sub>4</sub> compounds were synthesized in the laboratory by mixing

analytical reagent  $\text{H}_3\text{BO}_3$  and solution phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and heating at 500 or at 800°C for 1 hour (Abat et al. 2014a).

### **5.2.2 Toxicity test**

The soil was a sandy loam from Bordertown (South Australia), with a pH in 0.01 M calcium chloride ( $\text{CaCl}_2$ ) of 5.12. The concentration of available B was determined using hot-water extraction (Bingham 1982) and was 0.26 mg/kg, which is considered deficient for most crops (Sims and Johnson 1991). Other physical and chemical properties of the soil are given in Table 1. A Petri dish with an internal diameter of 9 cm was filled with about 50 g of soil moistened to field capacity. Canola seeds were sterilized by soaking in 0.04 M sodium hypochlorite ( $\text{NaOCl}$ ) for 15 min, rinsed three times with deionized water and air-dried at room temperature. About one gram of the sterilized canola seeds were weighed into a container. Another 10 g of the moistened soil was added to the seeds and mixed thoroughly. The soil and seed mixture was then spread evenly onto the soil in the Petri dish. A 30-mg fertilizer granule was placed at a depth of about 0.5 cm in the centre of the dish and the weight of the Petri dish recorded. The lid was then put on and the Petri dish transferred to a controlled environment room. The temperature of the room was 23–24 °C during the day and 15–16 °C during the night. A no fertilizer and MAP-only treatment were also included. All treatments were replicated five times. The soil was consistently kept moist near field capacity to ensure seed germination. The light was kept on for a period of 12 h per day and the light intensity was  $232 \mu\text{mol m}^{-2}\text{s}^{-1}$ . When the seedlings started to emerge (on the third day), the Petri dish lid was removed. Soil water content was maintained near field capacity by watering twice daily.

On the seventh and twelfth day, photographs of the growing seedlings were taken. The percentage of vegetation coverage was determined with image analysis software

(GIMP 2.8). The original images were decomposed (YCbCr ITU 470) and a threshold function was applied to the redness layer to convert the images to black (vegetated) and white (non-vegetated), after which the area of the vegetated zone was quantified (Fig. 5).

### *Soil analysis*

At the end of the 12-day experiment, the soils were air-dried and the B concentrations in soil sections around the granule application site were determined in hot-water extracts for the treatments with the granules with 2% B, MAP without B and the control (blank). The soil in the Petri dish was sampled in three concentric sections: less than 7.5 mm (corresponding to 1.7 g soil), between 7.5 and 15 mm (corresponding to 5 g soil) and further than 15 mm from the fertilizer application site (corresponding to 53 g soil). Five grams of soil (less for the inner section) were weighed into a centrifuge tube and 20 mL of boiling deionized water was added and shaken for 1 h. The suspension was filtered through Whatman No. 42 filter paper. Boron concentration in the filtrate was then analyzed using inductively coupled plasma – optical emission spectroscopy (ICP-OES) 7300 DV (Perkin Elmer).

### *Data analysis*

To relate the hot-water extractable concentration to the toxicity results (area of the non-vegetated zone), a diffusion profile was fitted to the hot-water extractable B experimental data, using following equation:

$$c_x = a.\text{erfc}(b.x) + c_{\text{bg}} \quad \text{Equation 1}$$

where  $c_x$  is the concentration of hot-water extractable B at distance  $x$  from the fertilizer application point,  $c_{\text{bg}}$  the concentration of hot-water extractable B for the

unamended soil (0.3 mg/kg) and  $a$  and  $b$  are fitted parameters. The complimentary error function (erfc) was used because it described the diffusion profile well. The parameters  $a$  and  $b$  were estimated by minimizing the residual squared error between predicted and measured concentration in each section.

Statistical analysis was conducted using Genstat 15<sup>th</sup> Edition SP2. Analysis of variance was performed to assess the effect of fertilizer source or B rate on the affected area. The differences between the means were evaluated using the Duncan Test for multiple comparisons at  $P \leq 0.05$ .

## **5.3 Results**

### **5.3.1 Seed emergence**

Clear differences in the toxicity symptoms were observed between the fertilizer treatments (Fig. 1). In the treatments using co-granulated ulexite, borax and colemanite, toxicity symptoms (yellowing and stunted growth) were already evident even in the 0.5% B treatments and became more severe with increasing B content in the fertilizer (Fig. 1). The canola seedlings treated with co-granulated  $BPO_4$  products displayed healthy growth without obvious visual toxicity symptom observed even at 2.0% B content (Fig. 1).

The non-vegetated area was derived through image analysis (Table 6). In the blank treatment, there was a small non-vegetated area due to incomplete coverage. The non-vegetated area was larger for the MAP (without B) treatment, indicating that the MAP fertilizer had a slight toxic effect on the seedlings. For the B treatments, the non-vegetated area generally followed the order: ulexite  $\geq$  borax  $\geq$  colemanite  $>$   $BPO_4$  and increased with increasing B concentration in the fertilizer. The non-vegetated area was significantly larger for MAP co-granulated with ulexite and colemanite at 1% and 2% B and co-granulated with borax at 2%B than for the MAP without B (Table 6).



However, there was no significance difference between MAP and MAP co-granulated with  $\text{BPO}_4$  at any of the B levels (Table 6).

### **5.3.2 Hot-water extractable B concentrations**

Hot-water extractable B concentrations around the fertilizer application site were higher for the products with ulexite, borax and colemanite (11-15 mg/kg in the inner section at <7.5 mm from the application site) than for those with  $\text{BPO}_4$  (2-8 mg/kg in the inner section) (Fig. 2).

A diffusion profile (Equation 1) was fitted to the measured concentrations. The radius of the affected area (1.6 to 1.8 cm for the fertilizer with 2%B as borax, ulexite or colemanite) was compared with the diffusion profile, which indicated a threshold of circa 8 mg B/kg (Fig. 2). In the treatments with  $\text{BPO}_4$ , the distance corresponding to a concentration of 8 mg B/kg was smaller than the radius of the non-vegetated area (circa 0.9 cm), indicating that the presence of a small non-vegetated zone was not related to toxicity of B, but to that of the MAP fertilizer itself (Table 6).

The total amount of added B recovered with the hot-water extraction was calculated by summing the hot-water extractable B amount recovered in the three sections (soil mass multiplied by the hot-water extractable concentration). The total amount of B recovered was significantly different between the soluble B sources and co-granulated  $\text{BPO}_4$  products (Table 3). Between 42 and 56% of the added B was recovered in hot-water extractable form for the soluble B sources (ulexite, colemanite, borax), compared to 16% for the co-granulated  $\text{BPO}_4$  500 °C and 3% for the co-granulated  $\text{BPO}_4$  800 °C.

## 5.4 Discussion

The results of this study showed that the application of co-granulated ulexite, borax and colemanite at time of seeding adversely affected germination and early growth of canola seedlings. On the other hand, canola seedlings treated with co-granulated  $BPO_4$  products did not display these negative effects.

Toxicity thresholds of around 5 mg B/kg (hot-water extraction) have been published for most crops (Cayton 1985; Nable et al. 1997). Mortvedt and Osborn (1965) found that root growth of oat and alfalfa was markedly decreased at hot-water B concentrations above 10 mg/kg. In this study, we found that the affected area corresponded to the zone with hot-water B concentrations  $>8$  mg B/kg at 12 days after the fertilizer application (Fig. 2). However, this should not be regarded as a toxicity threshold, since the B concentrations around the granule are not constant in time. Concentrations near a granule with soluble B are initially very elevated, but reduce over time as diffusion progresses (Mortvedt and Osborn 1965).

Toxic effects of soluble B fertilizers in the field have frequently been observed. The application of borax fertilizers, a soluble B source, has caused severe injury to crops grown in coarse-textured soils (Winsor 1950). Ozturk et al. (2010) found that the application of borax fertilizer broadcast at 15 kg B/ha in field experiments reduced the seed yield of eight canola cultivars by 31% on average. Banding of B fertilizer can be advantageous if the concentrations are within the acceptable range and the seed is placed adequately away from the band (Hughes-Games 1991), as it can be more effective in delivering B to the root. . However, the risk of B toxicity is higher with banded B fertilizer. For instance, considering 30-mg granules with 2% soluble B, an application rate of 1.5 kg B/ha corresponds to 2.5 granules per  $dm^2$  or an average distance between granules of circa 6.3 cm. However, when banded with the seed, the

distance between granules would be much smaller, and the likelihood of seeds being within a distance that would harm the seedling (here found to be circa 2 cm for canola) would be much higher.

The use of less soluble B sources is expected to eliminate or reduce the risk of B toxicity to crop seedlings. Colemanite applied in pure form has been regarded as a slow-release B fertilizer reducing risk of toxicity. Wear and Wilson (1954) reported that water soluble B extracted from colemanite was five times less than from borate, and it required twice as much colemanite as borate to produce the same toxicity effect. Because it is difficult to separately apply low rates of pure B fertilizers, B fertilizer is usually applied either blended or co-granulated with macronutrient fertilizers. Co-granulated fertilizer allows for a better field distribution of the B. However, when co-granulated with MAP, the low pH and high P concentrations (reducing Ca activities) render colemanite almost as soluble as ulexite and borax (unpublished data, 2014). Here, we showed that the toxicity effect of MAP co-granulated with B was similar for colemanite, ulexite and borax. In contrast,  $BPO_4$  still acted as a slow-release B source when co-granulated with MAP, and did not increase toxicity compared to MAP without B. In a recent pot trial study, we assessed the response of canola to these fertilizers under leaching conditions in two consecutive crops (Abat et al. 2014b). While the more soluble B sources induced B toxicity in the first crop and B deficiency in the second crop, the co-granulated  $BPO_4$  fertilizer provided adequate B supply for both crops.

The application of co-granulated borax, ulexite and colemanite at planting clearly has disadvantages for crop seedlings and could be potentially toxic even at low application rates. Predicting the rates at which toxicity may occur is difficult, as this depends on soil characteristics, environmental conditions and crop species. Use of

BPO<sub>4</sub> as a B source in NPK fertilizer is likely to be a seedling-safe alternative. Further studies in field experiments are required to assess the effectiveness of BPO<sub>4</sub> as a slow-release B fertilizer.

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### Figure captions

**Fig. 1** The original pictures of the Petri dishes with MAP+B fertilizer applied in the centre, at seven days after fertilizer application and seeding of canola (top) and the same pictures after image processing (one of five replicate shown for each treatment).

**Fig. 2** Hot-water extractable B concentration at 12 days after fertilizer application as a function of distance from the granule, for MAP granules co-granulated with 2% B as (A) ulexite, (B) borax, (C) colemanite, (D)  $\text{BPO}_4$  500 °C and (E)  $\text{BPO}_4$  800 °C. The dashed lines show the measured concentrations and the full line shows the diffusion profile (Eq 1) fitted to the measurements. The cross in panels (A-C) gives the radius of the non-vegetated zone.

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Table 5 Selected properties of the Bordertown soil.

<b>Parameter</b>	<b>Value/Concentration</b>
pH (0.01 M CaCl <sub>2</sub> )	5.12
Exchangeable Ca (cmol(+)/kg)	3.00
Exchangeable Mg (cmol(+)/kg)	0.98
Exchangeable Na (cmol(+)/kg)	0.24
Exchangeable K (cmol(+)/kg)	0.43
Cation exchange capacity (cmol(+)/kg)	8.50
Total B (mg/kg)	64
Hot water extractable B (mg/kg)	0.26
Organic carbon (%)	2.00
Clay (%)	8.40
Silt (%)	3.80
Fine sand (%)	72
Coarse sand (%)	11



Table 6 The non-vegetated area (in cm<sup>2</sup>) around MAP+B fertilizer granules depending on B source and B concentration in the granule. Also a blank (no fertilizer) and MAP without B treatment were included.

Fertilizer source	Boron rate			Rate Effect
	0.5% B	1.0% B	2.0% B	
None	0.8b	0.8d	0.8c	na
MAP	2.7ab	2.7c	2.7b	na
MAP+ulexite	6.1aB	6.6aB	9.9aA	*
MAP+borax	5.0aB	4.2bcB	9.5aA	***
MAP +colemanite	4.2aB	5.5abB	8.5aA	**
MAP+BPO <sub>4</sub> 500 °C	2.6ab	3.0c	4.3b	ns
MAP+BPO <sub>4</sub> 800 °C	2.7ab	3.2c	2.8b	ns
Source Effect	**	***	***	

Means followed by different lowercase letters indicate significant ( $P \leq 0.05$ ) differences within the column (source effect); means followed by different uppercase letters indicate significant differences within the row (rate effect);

ns: not significant; \*\*\*, \*\*, \*: significant at  $P \leq 0.001$ , 0.01 and 0.05 respectively; na: not applicable.

Table 7 Percentage of added boron recovered as hot-water extractable B in each soil section (at <7.5 mm, 7.5–15 mm or >15 mm of the fertilizer application point) or in the whole soil

<b>Co-granulated product</b>	<b>Added B recovered as hot-water extractable B (%)</b>			
	<b>&lt; 7.5 mm</b>	<b>7.5–5mm</b>	<b>&gt;15 mm</b>	<b>Total</b>
Ulexite	4.1a	8.5a	43.8a	56.4a
Borax	3.6a	7.1a	40.5ab	51.2ab
Colemanite	3.2a	6.0a	32.7b	41.9b
BPO <sub>4</sub> 500 °C	2.4a	2.6b	11.1c	16.0c
BPO <sub>4</sub> 800 °C	0.58b	0.57c	1.85d	3.0d

Different letters indicate significant ( $P \leq 0.05$ ) differences within the column.

The values are means of five replicates.

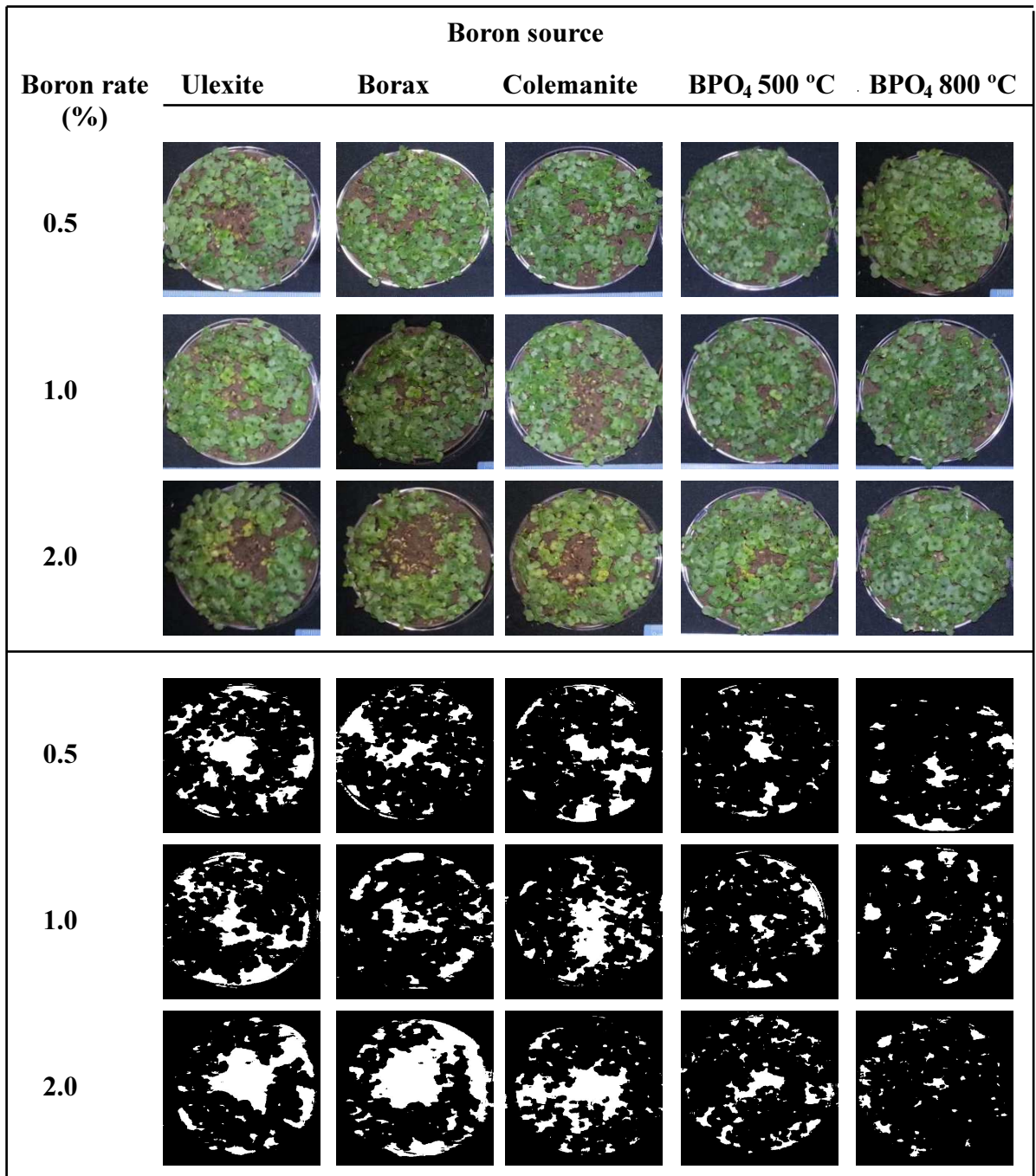


Fig. 5

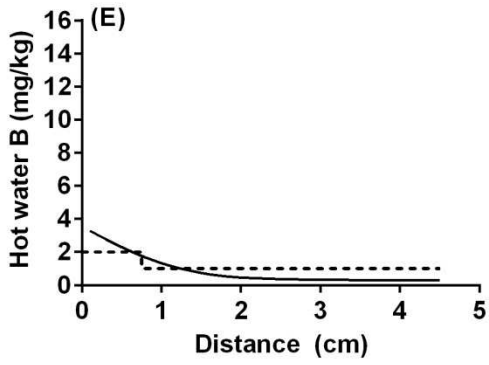
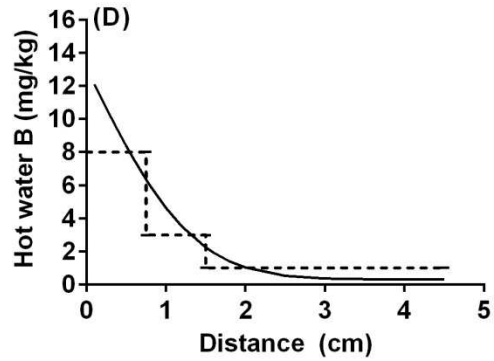
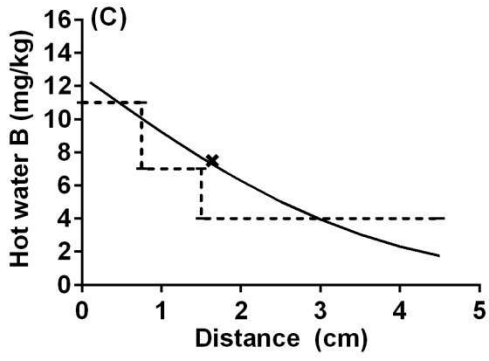
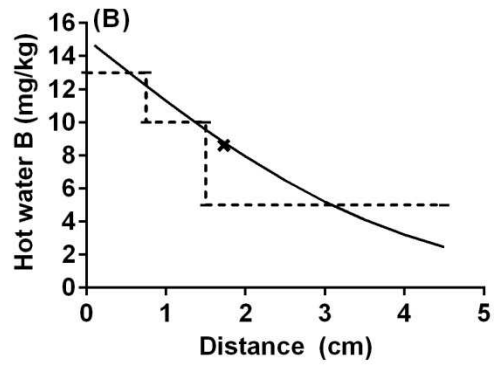
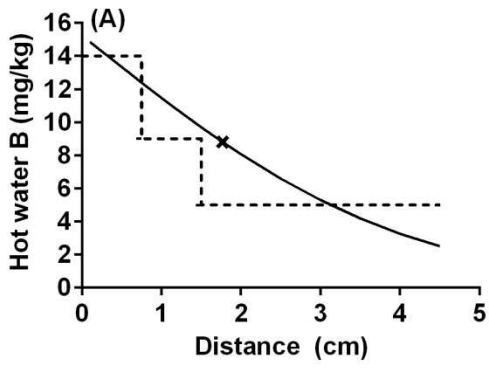


Fig. 6

**Responses of canola to the application of slow-release boron fertilizers and their residual effect**

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**STATEMENT OF AUTHORSHIP**

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**Margaret Abat (Candidate)**

Designed and conducted all research experiments, analyzed and interpreted the data, drafted the manuscript and acted as the corresponding author.

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Date: 1<sup>st</sup> December 2014

**Fien Degryse**

Contributed to the research ideas and design. Supervised the research work, helped with the data interpretation and provided critical evaluation of the manuscript.

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Date: 1<sup>st</sup> December 2014

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Contributed to the research ideas and design. Supervised the research work, helped with the data interpretation and provided critical evaluation of the manuscript.

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Date: 1<sup>st</sup> December 2014

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Contributed to the research ideas and design. Supervised the research work, helped with the data interpretation and provided critical evaluation of the manuscript.

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## **7.1 Introduction**

Water soluble boron (B) sources can only provide short-term relief and protection against B deficiency. This is because under high rainfall conditions, soluble B sources are leached from soil to an extent that an adequate supply of B is not maintained in the root zone throughout the growing season of many crops. Moreover, these highly soluble sources pose an increased risk of B toxicity to seedlings immediately after planting. These considerations prompted me to investigate and examine the possibility of using different B compounds to formulate slow-release B fertilizers.

## **7.2 Major Findings**

### **7.2.1 Co-granulated boron phosphates (BPO<sub>4</sub>) with mono-ammonium phosphate (MAP) as slow-release B fertilizers**

Although boron phosphate (BPO<sub>4</sub>) has been known for a very long time and is widely used as a catalyst, phosphating agent or an insulator, in many organic chemical reactions and manufacturing processes (Baykal et al., 2001; Hutchings et al., 1994; Vasovic and Stojakovic, 1997), there are no reports of it being used commercially in agriculture. It has been suggested that BPO<sub>4</sub>, when applied to the soil, may slowly dissolve and provide B for plants (Magda et al., 2010). However, no systematic and detailed study has been conducted to test the suitability of this material as a B compound for co-granulation with macronutrients. The solubility of BPO<sub>4</sub> compounds can be modified by synthesizing the compound at different temperatures and heating times. In this study, BPO<sub>4</sub> was synthesized using the simple and effective method of mixing boric acid (H<sub>3</sub>BO<sub>3</sub>) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and heating at temperatures between 25 and 1000 °C for 1 or 24 h. The properties of BPO<sub>4</sub>



synthesized over this range differed markedly. Boron phosphates synthesized at 300 °C and below were highly soluble and hygroscopic, whilst those synthesized at 1000 °C were quasi insoluble. Thus, these products were considered unsuitable for co-granulation and were not tested further.

In contrast,  $BPO_4$  synthesized at 500 and 800 °C were non-hygroscopic, free-flowing, and had intermediate solubility. The water solubility of these compounds was low at product (non-adjusted) pH and at pH ~5 as compared with the commercial B sources, namely borax, ulexite and colemanite, suggesting they may provide a slow-release benefit. The column dissolution study showed the B release from  $BPO_4$  500 °C for 24 h and 800 °C for 1 h compounds was slower than most of the commercial B sources. Although  $BPO_4$  synthesized at 500 °C for 1 h was soluble in water and B concentration in the leachate could be potentially toxic to seedlings, this compound was preferred to  $BPO_4$  synthesized at 500 °C for 24 h for co-granulation with macronutrient fertilizers because it can save cost in term of shorter preparation time. Hence, the characteristics possessed by  $BPO_4$  synthesized at 500 and 800 °C fulfilled the criteria for slow-release B fertilizer sources including moderate to low water solubility leading to slow B release and low toxicity risk, thus making them potentially viable as raw materials for co-granulation.

The application of B co-granulated with macronutrient fertilizer is preferable to separate application of pure B sources alone or as a bulk-blend. The benefits of granulation are: improved handling and compression characteristics of fine powders; control of the dissolution of key ingredients in a mixture; and minimization of segregation potential of a blend consisting of various ingredients (Bilgili et al., 2011).

The solubility of  $BPO_4$  co-granulated with the common phosphorus fertilizer, MAP, was lower than for borax, ulexite and colemanite co-granulated with MAP. In a soil column study, B concentrations in the leachate of co-granulated borax, ulexite and colemanite were

elevated immediately after fertilizer application and exceeded the toxicity level for most crops. On the other hand, B released from the co-granulated  $BPO_4$  products was below the toxicity threshold; and B release was more sustained than borax and ulexite, indicating the potential for  $BPO_4$  to provide an extended supply of B at low concentrations. This ability to provide a continuous supply of B is of utmost importance for plant growth, especially later in the plant growth cycle i.e. at flowering, since B is immobile in many plant species.

The increase in solubility of colemanite and ulexite found when co-granulated with P (MAP) limits the use of these materials in any potential slow-release B formulation. Since this limitation does not apply to  $BPO_4$ , the co-granulated  $BPO_4$  products are expected to increase B fertilizer use- efficiency, especially in high rainfall areas.

### **7.2.2. Co-granulated $BPO_4$ products are safe for crop seedlings**

Boron toxicity to sensitive crops can occur due to excessive applications of fertilizer B or the use of irrigation water containing high concentrations of B (Gupta et al., 1985). In addition, banding B fertilizer either with, or close to, seeds has greater potential to result in B toxicity than broadcasting (Martens and Westermann, 1991).

The placing of borax, ulexite or colemanite co-granulated with MAP in close proximity to canola seeds resulted in B toxicity to the emerging seedlings. With these B sources, toxicity symptoms were already evident at low B contents in the fertilizer (0.5% B) and the toxicity effect became more severe with higher B content in the fertilizer. The concentrations of hot-water extractable B in soil around the granules supported the toxicity results, with toxic concentrations in close proximity to the granule for the most soluble B sources. In comparison, no toxicity symptoms were observed even at the highest B content (2.0%) with the application of co-granulated  $BPO_4$  products (Chapter 5).

The application of co-granulated soluble B sources at planting clearly has concerns from a toxicity perspective even at low application rates. However, predicting the rates at which toxicity may occur is difficult, as this depends on soil characteristics, environmental conditions and crop species. Based on my observations, co-granulated BPO<sub>4</sub> products are likely to be a seedling-safe alternative.

### **7.2.3 Direct and residual effects of co-granulated BPO<sub>4</sub> products**

Crop response to B is generally found in the form of increased crop yields and/or improved quality (Gupta, 1993). These responses were studied in a pot trial with two successive canola crops, to assess the difficulties associated with B fertilizer management (leaching losses, B toxicity) related to the use of soluble B sources and to investigate the usefulness of BPO<sub>4</sub> as a slow-release alternative.

In the absence of B fertilizer, plant growth was delayed; and B concentrations (<30 mg B/kg) in the plant tissues were lower than levels considered adequate for canola. The application of MAP co-granulated with soluble B sources (ulexite, borax and colemanite) reduced canola shoot dry weight and the plants displayed some toxicity symptoms such as burning (necrosis and chlorosis) at the edges of the older leaves. The B concentrations in the plant shoots of these plants ranged from 97 to 108 mg B/kg; potentially toxic concentrations for canola plants. Even more severe B toxicity was prominent with the application of pure B compounds (not co-granulated with macronutrient fertilizer). Conversely, the B concentrations in the plant tissues were within the adequate range for canola (35-80 mg B/kg) (Reuter and Robinson, 1997) for the treatments with co-granulated BPO<sub>4</sub> and the plants showed no signs of toxicity.

While the application of co-granulated soluble B fertilizers caused toxicity problems in the first crop, leaching of the soils removed most of the added B resulting in deficiency for the subsequent crop. Detrimental effects such as stunted growth, delayed flowering, aborted

flowers and empty pods were observed in the second-crop plants treated with these co-granulated soluble B sources. In contrast, the second-crop canola plants treated with co-granulated  $BPO_4$  products did not display any deficiency symptoms. These results suggest that a single application of MAP co-granulated with  $BPO_4$  would remain effective for at least two canola crop seasons in a high leaching environment. In summary, the efficacy of the co-granulated  $BPO_4$  products was attributed to the provision of slow-release B over multiple crop cycles.

The production costs required to manufacturing a slow-release B fertilizer by first producing  $BPO_4$  and co-granulating with MAP is expected to be higher than for the conventional soluble B sources. However, since the potential benefits of the utilization of these products include reduction in application costs (less frequent application compare to soluble sources), improved nutrient-use efficiency, less negative environmental effects and savings in labour, the economic implication of the use of  $BPO_4$  fertilizers needs to be carefully evaluated against other B products. The benefits may well justify their use in future agricultural production especially in high rainfall areas.

### **7.3 Contribution to Knowledge**

The research reported in this thesis was designed to study and examine  $BPO_4$  compounds synthesized at different temperatures and heating times for use as raw materials in slow-release B fertilizers; to determine the suitability of these compounds and other B sources for co-granulation with macronutrient fertilizers; and to determine the effectiveness of the co-granulated B fertilizers on crop performance (both deficiency alleviation and prevention of B toxicity). The new contributions to knowledge of this thesis are:

1. Discovery that  $BPO_4$  compounds synthesized at 500 and 800 °C are viable as raw materials for slow-release B fertilizers and are suitable for co-granulation with MAP.

2. Development of a novel toxicity test to assess B toxicity in crop seedlings. This method can be applied to test the toxicity of other fertilizers to crop seedlings at germination and early growth.
3. Improved understanding of the behavior of other slow-release B sources, namely ulexite and colemanite, either as pure compounds or co-granulated with MAP. To my knowledge, no study has been attempted to co-granulate either ulexite or colemanite with MAP, examine their B release rates and assess their effectiveness for crop growth. Such understanding has practical value, since application of B co-granulated with macronutrient fertilizer is preferable over application of the pure compound, but this can affect the release characteristics.
4. Development of a slow-release B fertilizer. The pot trial results indicated that MAP co-granulated with  $\text{BPO}_4$  provided B in adequate amounts over two crop cycles under high-rainfall conditions.

#### **7.4 Future Research**

The results of this study raised several new scientific questions and identified gaps in our knowledge that require further investigation.

1. The plant uptake experiments (direct and residual effects of fertilizer B) were conducted under controlled environment conditions. The results obtained from the pot experiments do not represent field conditions. Therefore, field experiments in various locations and conditions are essential for identifying the appropriate fertilizer rates before recommendations for commercial production are made, and to validate that the products made with  $\text{BPO}_4$  are superior to products co-granulated with other available B sources (e.g. borax, ulexite, colemanite).

2. Research into the length of any residual effect of soil applied slow-release B is also important in determining the B requirements of subsequent crops. This information could be very useful in the planning for crop rotation and deciding which crops to grow.
3. It would be worthwhile to investigate the effectiveness of polymers like polyethylene, polyvinyl acetate, resins and surfactants for coating soluble B sources. It has been shown that coating of NPK fertilizers with polymers and resins reduced the nutrients release rates and are successful in controlling product longevity and efficiency, albeit at a high cost.
4. The application of the toxicity test to measure the seedling of fertilizers could be extended to test a wide range of other crops and fertilizers, to derive plant-specific 'salt indices' of fertilizers under more relevant conditions (using fertilizer granules) than the current determination of salt index.
5. In this study, the granule strength, abrasiveness or dust generation from the co-granulated B sources has not been measured. For future research, these parameters should be tested and analyzed. This information is important as the granules should survive mechanical stresses involved during handling, storage and transportation.
6. Research is needed on the rate of nutrient release from the slow-release  $BPO_4$  products under more relevant water balance conditions e.g. in field lysimeters and the factors (e.g. water flow, soil properties) that affect the release rate should be explored. The information will enhance our understanding of these products, and could improve fertilizer management strategies and increase B use-efficiency.

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Supporting information for Chapter 3: Formulation, synthesis and characterization of boron phosphate (BPO<sub>4</sub>) as raw materials for slow-release boron fertilizers



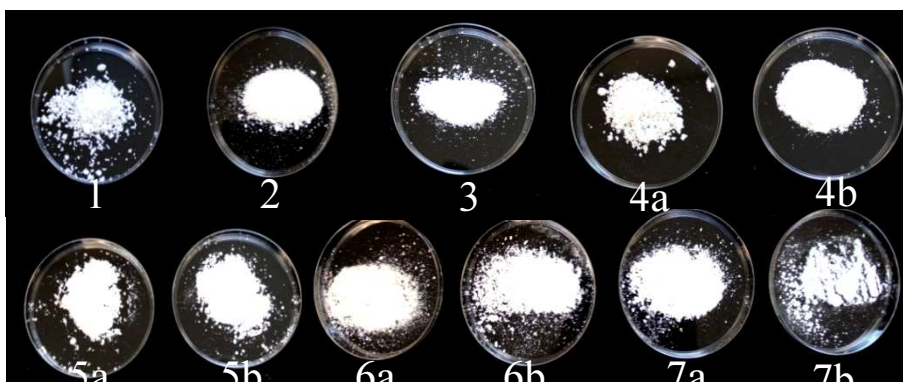


Figure A7-1 Boron phosphate ( $BPO_4$ ) compounds synthesized at: (1) 25 °C (168 h), (2) 100 °C (72 h), (3) 150 °C (1 h), (4a) 300 °C (1 h), (4b) 300 °C (24 h), (5a) 500 °C (1 h), (5b) 500 °C (24 h), (6a) 800 °C (1 h), (6b) 800 °C (24 h), (7a) 1000 °C (1 h), (7b) 1000 °C (24 h). The images are representative of triplicate.  $BPO_4$  compounds synthesized at 300 °C and below were hygroscopic and clumped together whilst  $BPO_4$  compounds synthesized at 500 to 1000 °C were non-hygroscopic and free-flowing.

## Appendix 2

The x-ray diffraction (XRD) patterns of the  $\text{BPO}_4$  compounds synthesized at 500, 800 and 1000 °C were the same but their crystallinities, as indicated by the peak intensities, were different. The intensities increased with increasing synthesis temperature and heating time, indicating the formation of more crystalline  $\text{BPO}_4$  at higher temperatures. All the peaks in the X-ray pattern were identical with those of reference  $\text{BPO}_4$  standard (green line) (Figures A2-1 to A2-6).

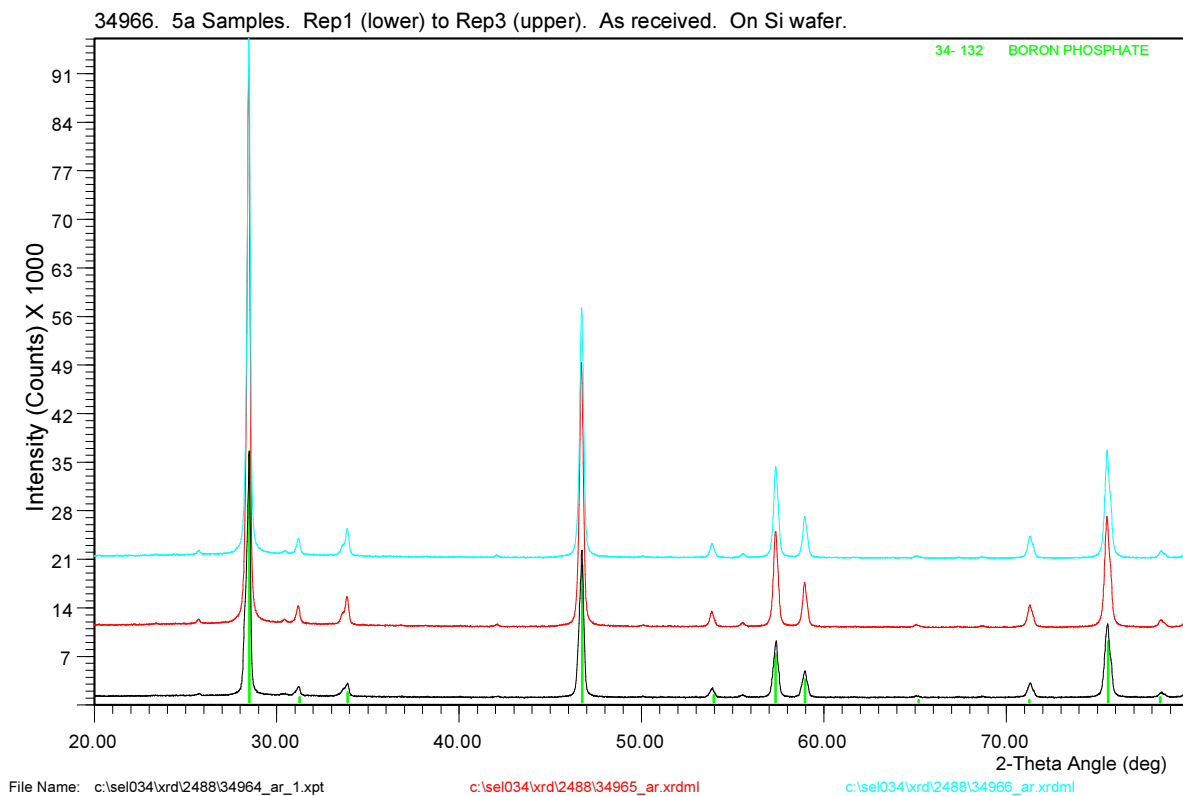


Figure A2-1 X-ray diffraction patterns of  $\text{BPO}_4$  compounds synthesized at 500 °C for 1 h.

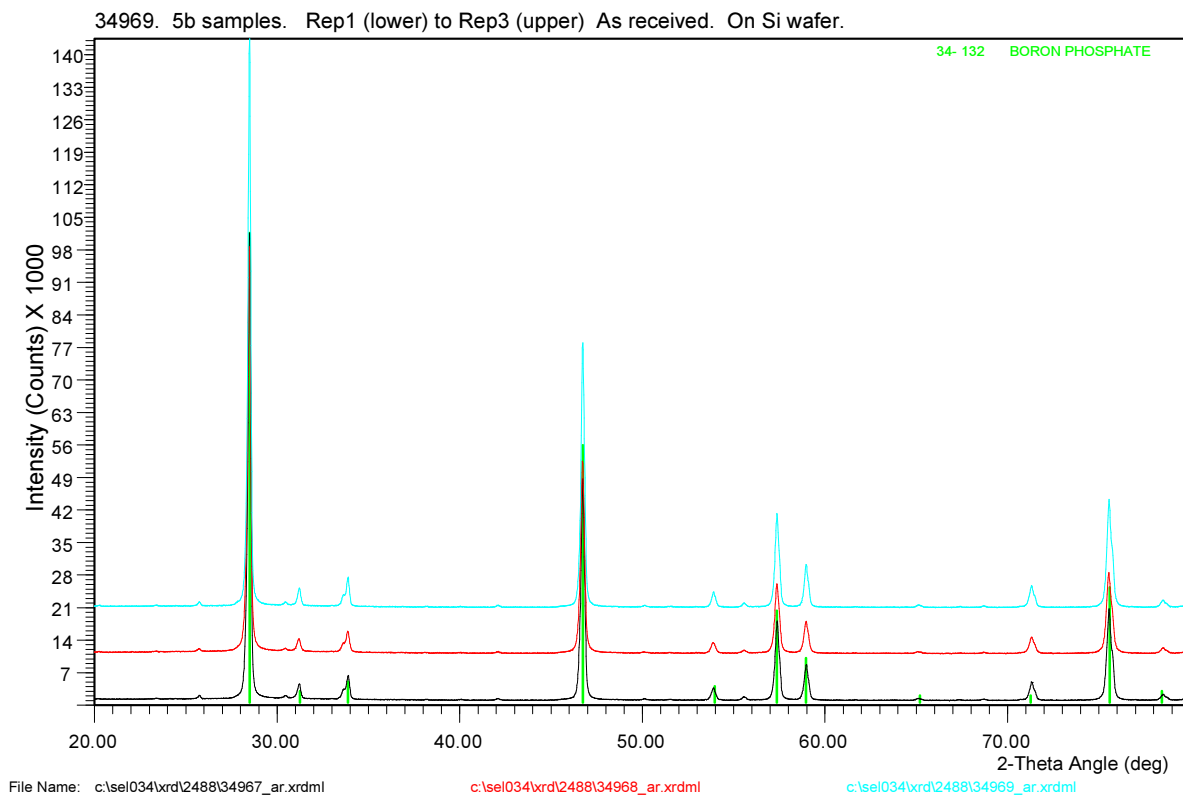


Figure A2-2 X-ray diffraction patterns of  $\text{BPO}_4$  compounds synthesized at 500 °C for 24 h.

34972. 6a samples. Rep1 (lower) to Rep3 (upper). As received. On Si wafer.

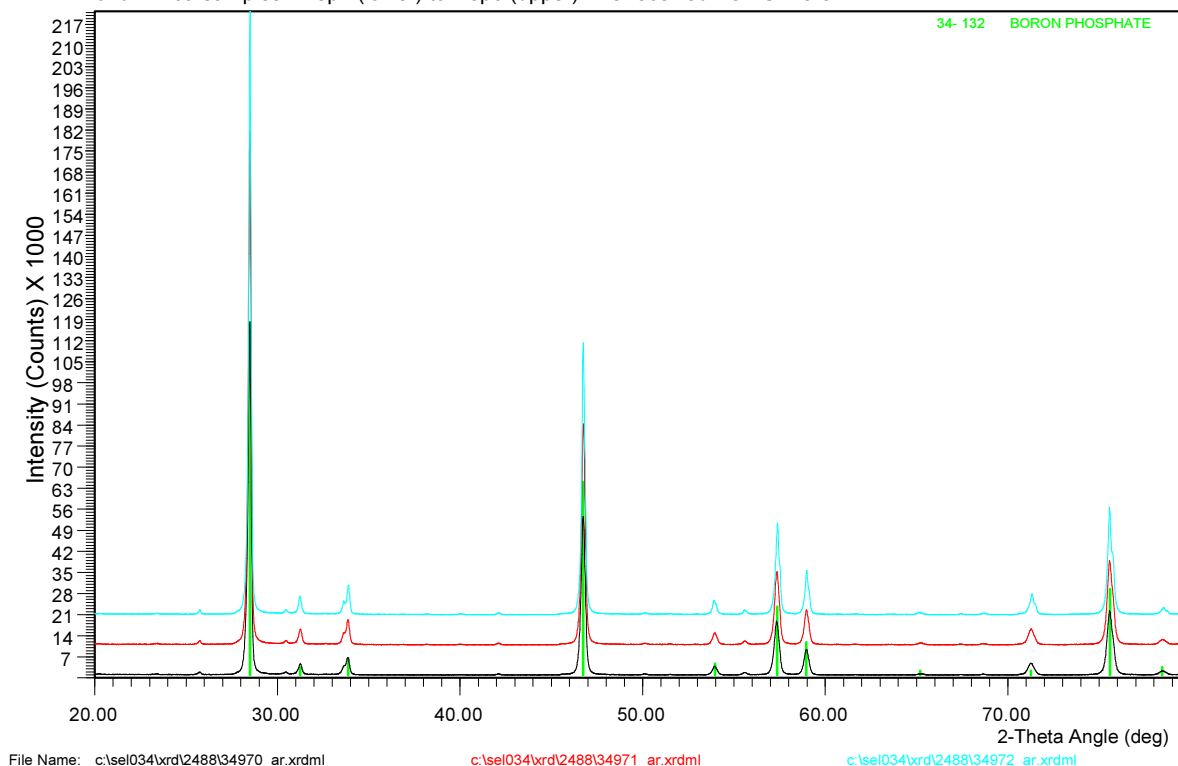


Figure A2-3 X-ray diffraction patterns of BPO<sub>4</sub> compounds synthesized at 800 °C for 1 h.

34975. 6b samples. Rep1 (lower) to Rep3 (upper). As received. On Si wafer.

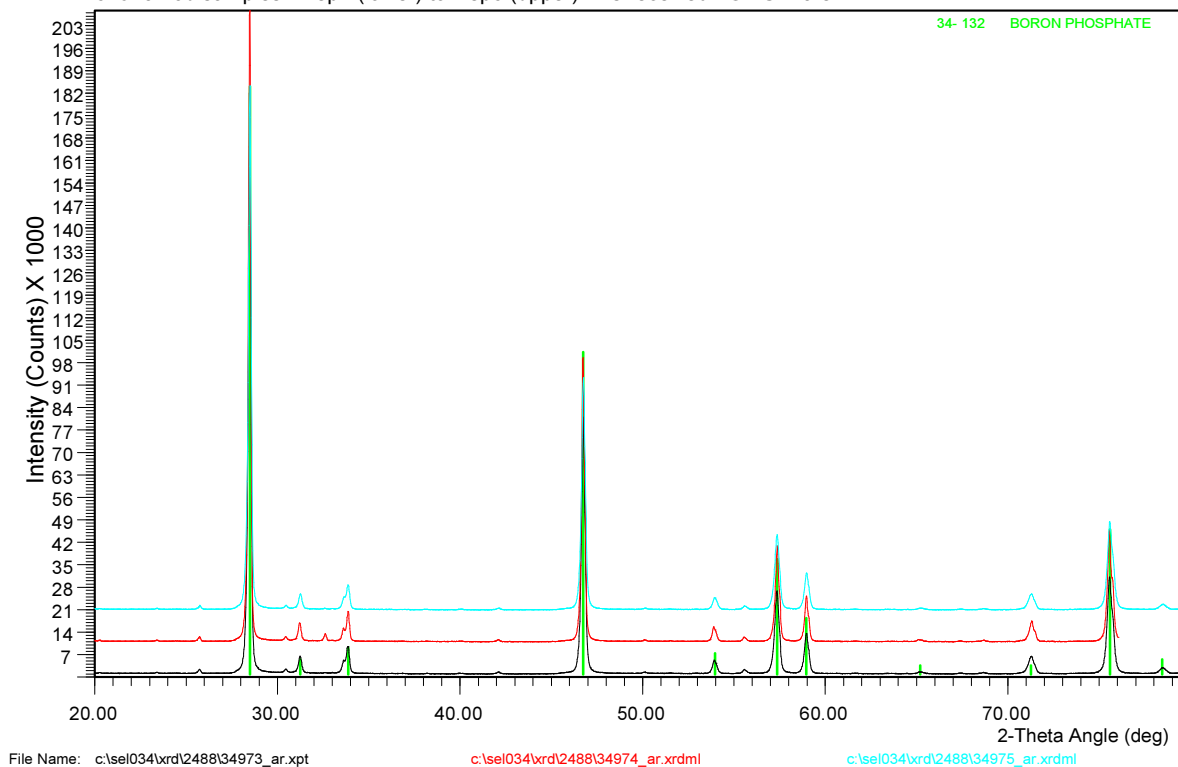


Figure A2-4 X-ray diffraction patterns of BPO<sub>4</sub> compounds synthesized at 800 °C for 24 h.

34978. 7a samples. Rep1 (lower) to Rep3 (upper). As received. On Si wafer.

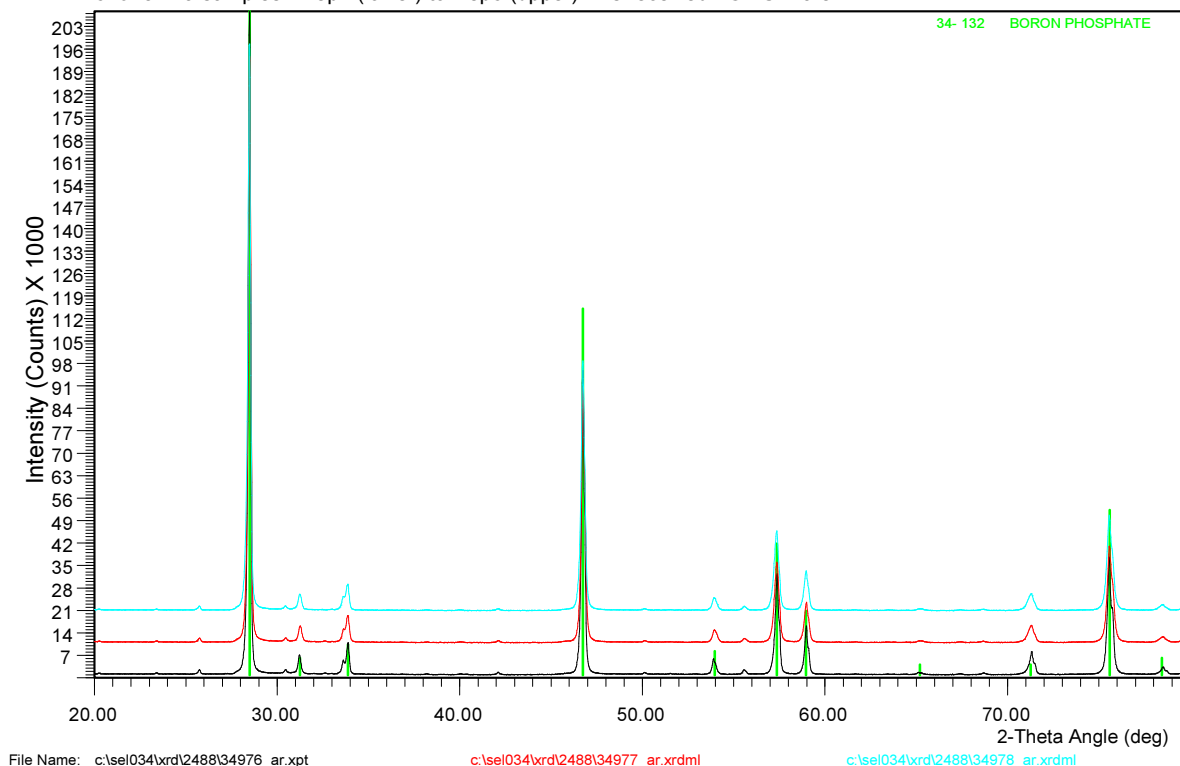


Figure A2-5 X-ray diffraction patterns of  $BPO_4$  compounds synthesized at 1000 °C for 1 h.

34981. 7b samples. Rep1 (lower) to Rep3 (upper). As received. On Si wafer.

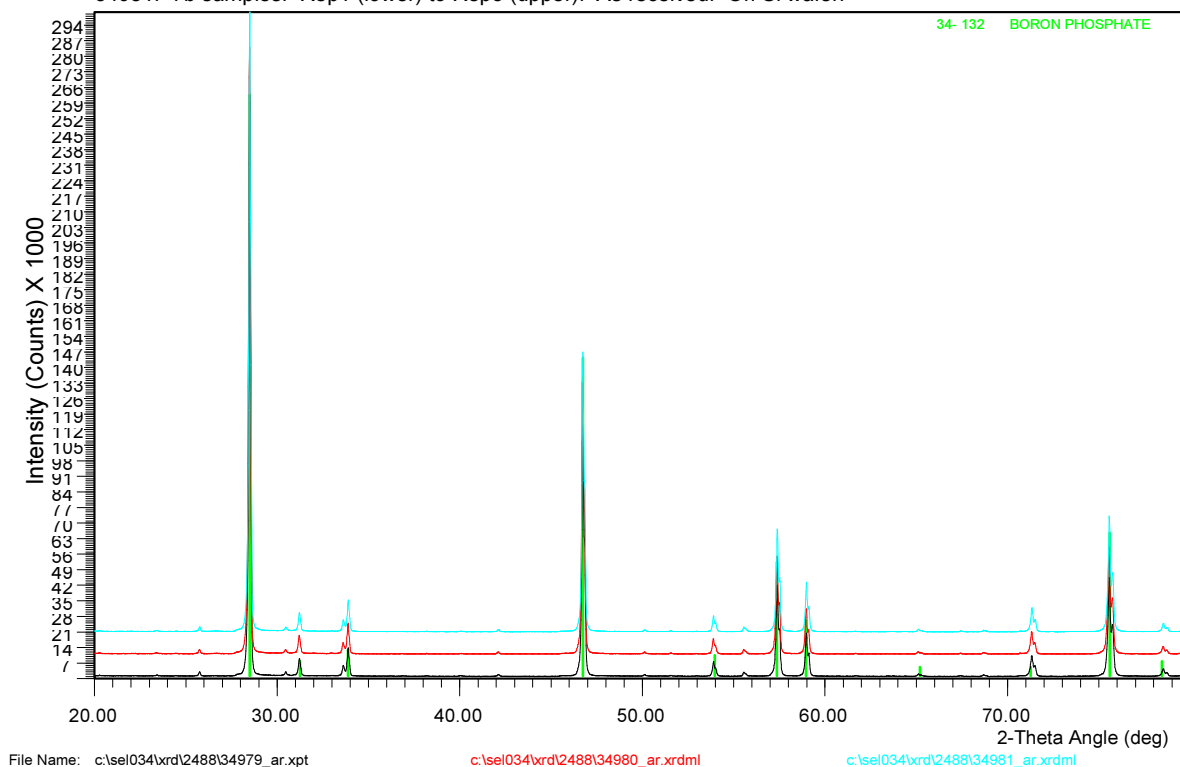


Figure A2-6 X-ray diffraction patterns of  $BPO_4$  compounds synthesized at 1000 °C for 24 h.