Boron uptake and distribution in canola grown on acidic soils amended with acidic and alkaline fly ashes

V. Manoharan[1*], I.A.M.Yunusa[1], R. Lawrie[2], M.D.Burchett[1], C.G. Skilbeck[1] and D.Eamus[1]

[1]Institute for Water and Environmental Resource Management and Department of Environmental Science, University of Technology, Sydney, P.O. Box 123, Broadway, NSW 2007, Australia. [2]NSW Agriculture, Department of Primary Industries, Locked Bag, Richmond, NSW 2753, Australia.

[*]Corresponding author:

E Mail: manoharan.veeragathipillai@uts.edu.au

Tel: (61) (2) 95148266

Fax: (61) (2) 95144079

Abstract

Phytotoxicity due to excessive boron (B) uptake by plants is a major impediment to routine agronomic utilisation of coal fly ash. Phytotoxicity may be minimised if fly ash is applied to discrete layers of a soil profile at rates that are agronomically realistic and where soil volume does not restrict root exploration. We tested this hypothesis in a glasshouse study by assessing 11 Australian fly ashes from which four were selected for further study; these four had pH of between 3.29 and 10.77, an electrical conductivity (EC) of between 1.1 – 19.1 dS/m and a total B content (B_t) of 12 – 127 mg/kg. These ashes were incorporated at rates equivalent to 0, 12,

36 and 108 Mg /ha into the top 10 cm of three acidic soils that were extracted as intact cores (100 cm long, 15 cm diameter)from three different field sites in New South Wales, Australia.. Canola (*Brassica napus* L.) was grown on the cores and the response of shoot growth and seed yield were measured, along with concentrations of B in plant tissues. In addition, concentration of B, pH and EC were measured in soil-leachate collected during the experiment. On average 20 – 30 % of B_t was hot-water soluble (B_s) in acidic fly ashes (pH <5), but only 5 – 10 % of B_t was hot-water soluble in the alkaline fly ashes. The EC, pH and B_t in the soil were significantly increased only in the zone to which the ash was incorporated. Accumulation of B in the shoot increased with rate of application of the ash, but the values were well below the phytotoxic threshold limit of 170 mg/kg. The amount of B derived from fly ash that was removed by the plant ranged from 1 to >100 % depending on the type and rate of ash application. The concentration of B in the leachate was highly variable but was generally less than 0.05 mg/L irrespective of fly ash treatment. The results from this experiment suggest fly ash-derived B may not be phytotoxic if the ash is applied at rates not exceeding 12 Mg/ha and incorporated into the top layer of the soil. Below these rates of application, ash would improve the supply of B and other plant nutrients, especially in acidic, nutrient-deficient, soils.

***Additional keywords*:** trace elements, boron toxicity, boron leaching, plant, acid soils

Introduction

Phytotoxicity and/or bioaccumulation due to the high content of trace elements in fly ash could

48 be a major limitation to a routine agronomic use of this industrial by-product as a soil
49 amendment. Boron (B) is often cited as the most phytotoxic trace nutrient in fly ash (Tolle *et*
50 *al*. 1983; Aitken and Bell 1985; Carlson and Adriano 1993) and this is because of its high
51 concentration and solubility, relative to other trace elements in coal fly ash (Plank and Martens
52 1974; El-Mogazi *et al.* 1988). Although B is an essential plant nutrient, it quickly becomes
53 toxic once its concentration in hot water- extractable form exceeds 5 mg/kg in soil (Keren and
54 Bingham 1985). A number of studies have reported poor growth and elevated B concentration
55 in tissue, even in the absence of overt symptoms of B phytotoxicity, when plants are grown on
56 soils treated with fly ash (Kukier *et al*. 1994; Sims *et al*. 1995). This makes it difficult to detect
57 and treat B toxicity to prevent reductions in plant growth and yield.
58
59 Phytotoxicity due to excessive accumulation of ash-derived B depends on properties of the fly
60 ash and those of the soil to which the ash is applied, and the crop type. Properties of the fly ash,
61 such as stage of weathering and pH affect B content and solubility (Hollis *et al*. 1988; Carlson
62 and Adriano 1993). Soluble B (B_s) could constitute as low as 1.5 % (Dreesen *et al*. 1977) to as
63 high as 64 % (James 1982) of the total B (B_t), depending on B_t and cation content of the fly ash
64 and pH of the leachate solution (Hollis *et al*. 1988; Kukier and Sumner 1996). Solubility of B
65 in the soil is controlled not only by the pH of soil, but by several other factors, such as the
66 amounts and type of clay, iron oxides and organic matter content (Keren and Bingham 1985).
67 Soils with high pH, clay and iron oxides tend to inhibit solubility of B; the trend is reversed in
68 soils having low pH and materials that adsorb B such as clay and iron oxides (Keren and
69 Bingham 1985).
70 Phytotoxicity due to B from fly ash application has been especially apparent in plants grown in
71 limited soil volumes and non-leaching conditions (Aitken and Bell 1985; Kukier *et al*. 1994;

Sims *et al*. 1995), possibly due to a build up of large concentrations of B in the rooting medium. Aitken and Bell (1985) reported reduced growth of 30 % in French bean (*Phaseolus vulgaris* L.) and ≥70 % for Rhodes Grass (*Chloris gayana* L.) due to B phytotoxicity arising from applications of high rates of unweathered fly ash in a glasshouse study. Similarly, under non-leaching conditions, Sims *et al*. (1995) reported that the concentration of B in corn (*Zea mays*) rose to phytotoxic levels when fly ash was applied at 40 % (w/w) of soil. Phytotoxicity due to B could be induced even by fly ash addition rates as low as 1.25 % when corn was grown in a limited soil volume under non-leaching conditions (Kukier *et al*. 1994). The phytotoxicity of B tends to be minimised, however, when fly ash is applied to crops in field studies (Cline *et al*. 2000; Clark *et al*. 2001). When fly ash was incorporated (at up to 625 Mg/ha) into the top 5 cm of soil found significant elevation of B accumulation, or reduced yield in canola (*Brassica napus*) only when rate of fly ash addition exceeded 125 Mg/ha (Yunusa *et al*. 2008). Similar results were reported by Cline *et al*. (2000) who found that fly ash applied to soil at rates as high as 50 Mg/ha caused no apparent B phytotoxicity in either field grown corn or soybean. Indeed the addition of fly ash increased yields by up to 35% compared with untreated controls. Adriano *et al*. (2002) also found no B phytotoxicity in turf grown on soil treated with fly ash at rates as high as 1,120 Mg/ha (~ 40 %) in a field study. Yunusa *et al*. (2008) argued that minimisation of phytotoxicity in the field and/or in large deep media was associated with the plant's ability to recover from any initial suppressed growth caused by excessive salt or elemental concentration in the treated top layers of the soil. They observed that once the roots extend beyond the zone of ash incorporation that plants were able to recover and often made up for the initial poor growth. This recovery is generally not possible in limited soil volumes.

In this paper we present results from a study in which we investigated B uptake and its

distribution in canola, and consequent growth and yield of the plant, on three acidic soils treated with four fly ashes. We also present data on B uptake by canola relative to B input from fly ash applied to the soil from a supplementary trial. We used these two data sets to test the hypothesis that B phytotoxicity is minimised when fly ash is used at modest rates and incorporated into the top layer of the soil. Our specific objectives were to: (1) chemically characterise selected Australian fly ashes to assess their capacity to supply B, (2) investigate uptake of B by canola supplied with variable types and rates of fly ash, and (3) quantify soil B accumulation and to evaluate the quality of leachate on the basis of its B concentration, salinity and pH.

2. Materials and methods

2.1 Fly ashes collection and chemical analysis

Fly ash was collected from 11 power stations that burn a range of coals under different operating conditions across Australia. Five of the ashes were strongly acidic (pH < 5), two slightly acidic (pH ~6) and the remaining four were alkaline (pH >8) (Table1). Two of the alkaline ashes (FA 8 and FA 9) were collected from power stations in Victoria, which burn brown coal, while the rest were from stations that burnt sub-bituminious or anthracite coal. The fly ashes had widely varying elemental concentrations as well as wide ranging EC values (0.14 to 19.06 dS/m). The salt content of ash derived from brown coal was extremely high due to high soluble salts of Na, K, Ca, and Mg. These also had very high concentrations of total Fe and Mn. For the greenhouse study, we selected only four fly ashes (FA 2, FA 4, FA 9, and FA 11) based on their chemical characteristics, mainly pH, B_t and EC values. Fly ashes FA 2 and

FA 4 had acidic pH and low B_s and B_t content while FA 9 and FA 11 had alkaline pH with high content of B_t. Compared with FA9, FA11 had extremely high salt content.

2.2 Soil selection and sampling

Three acidic soils were collected in intact cores from farmlands at Kangaloon (34.3º S, 150 3º E) and Menangle (34.3 º S, 150 41 º E) and from a logged pine forest in the Belanglo forest reserve (34.6º S, 150.4º E) in eastern New South Wales, Australia. Intact soil cores were extracted inside polyvinyl chloride (PVC) tubes (100 cm deep and 15 cm internal diameter) with a ProLine hydraulic corer mounted on a truck. Soil samples taken from the top 25 cm of each soil type were used to characterise the chemical properties of the top soil layer. These soil samples were air dried, passed through a 2 mm-screen and mixed thoroughly. Selected chemical characteristics of the three soils were determined as listed in Table 2. The three soils included one sandy clay loam soil with gravely subsoil (Belanglo) and two clay loams with clay subsoils (Menangle and Kangaloon). All three soils were acidic in nature, had a low EC and low total and Hot-water soluble B (B_s) content (Table 2). Belanglo and Kangaloon soils were deficient in P, with the Colwel-extractable P contents of 8 and 27 mg/kg respectively. These values are considered to be well below the desirable level of 45-50 mg/kg for crop growth in a light to medium textured soil (Rayment and Higgins 1992). In contrast, the Menangle soil had an extremely high Colwel-extractable P of 199 mg/kg.

2.3 Treatments and experimental design

Thirteen treatments were imposed on each soil type, comprising the four ash types applied at

three rates 12, 36 or 108 Mg/ha and a control (0 Mg/ha ash). Each treatment was replicated in three soil columns, which were then arranged on benches in a completely randomized design. In all cases fly ash was mixed thoroughly into the top 10 cm of soil. The cores were then planted with eight seeds of canola (*Brassica napus. L*) cv. Surpass 603CL (Pacific seeds, Toowoomba, Australia) at approximately 20 mm depth.

2.4 Measurements and analyses

Plant growth, harvesting and analysis

One week after emergence the seedlings were thinned to 4 plants per core, and later to 2 plants at start of flowering, which was about 12 weeks after sowing. Canola shoots and seeds were harvested at maturity. Both pods and shoots were weighed, after drying in a forced air oven at 60^{o}C for three days. Dried plant samples were ground in a stainless steel grinder and sub-samples taken for chemical analysis. Grounded shoot and seed material was weighed (0.4 g) into separate Teflon containers, digestion solution (4 ml of 15.6 M HNO_3 + 0.5 ml 12 M HCl + 2 ml H_2O_2 (30 %) was added, and containers were left for 20 minutes inside the fume hood before placed in high pressure (40 bar) closed microwave digestion vessel (Anton Parr-Multiwave 3000). These samples were microwave digested for 20 minutes with a maximum power of 1400 W. Digested solutions were brought to a final volume of 100 ml with deionised water. Solutions were filtered with through a 0.45 µM Millipore® syringe cellulose nitrate filter disk and stored in plastic containers in a cold room (4^{o}C) until analysed for B and other minor and major elements by ICP-MS.

Leachate sampling and analysis

Plants were watered regularly and leachate was captured in collecting jars by means of tubes pre-installed through the bottom caps of the cores. The leachate was removed periodically for analysis. The first leachate accumulations were removed for analysis 10-days after watering, and were then collected when enough leachate had accumulated for complete chemical analysis. When the leachate was collected, all leachate volumes were recorded and leachates were analysed for pH and EC immediately with the exception of the first leachate, which was inadvertently treated with HNO_3 prior to pH and EC measurements and so data for these two variables are not presented for this first leachate. Samples were preserved with Analytical grade concentrated HNO_3 and kept in a cold room at 4 ^{o}C until subject to chemical analysis. Leachate samples collected prior to flowering (14 June 2005– 28 August 2005) and after flowering (9 September 2005–19 October 2005) were combined to make two separate composite leachate samples and 15 ml of the sub-sample was filtered with 0.45 µM Millipore® syringe cellulose nitrate filter disk prior to elemental analysis. All elements were analysed either by ICP-OES or ICP-MS.

Soil sampling and analysis

To further investigate the fate of ash-derived B in the soil cores and to augment the findings from the leachates, soil cores from light-to-medium textured Belanglo soil (sandy clay loam soil) was selected to determine the soil chemical changes and distribution of B through the profile. Soil cores from Kangaloon and Menangle were not divided as these cores were replanted with beans to further study the residual effects of fly ash application. After harvest, the soil cores were covered with plastic sheets to minimize moisture loss and were stored in a

cool dark room prior to further testing. The cores from Belanglo soil were longitudinally split into two halves and composite moist soil samples of 250 g were taken from one half of each core at five depth intervals: 0-10, 10-20, 20-40, 40-60 and 60-100 cm. These samples were analysed for pH and EC in 1:5 soil/water (w/v) suspensions, and total elements, including B. Total elemental analysis involved air-drying the soil samples followed by another drying at 60 ^{o}C for 24 hours before being fine ground. Samples of 0.5 g of soil/fly ash were microwave digested in concentrated HNO_3 according to US-EPA 3051 method.

Extractable P, in 1.0 g samples of fly ash shaken at room temperature for 16 h in 100 ml of 0.5 M $NaHCO_3$, (Colwell 1965; Rayment and Higginson 1992), was measured by colorimetric method (Murphy and Riley 1962). Water soluble cations were measured in the 1: 6 ash: water (w/v) extracts. Total C and organic C were determined according to standard procedures with an automated LECO truSpec C and N analyser. Hot -water soluble B was determined by boiling 10.0 g samples in 20 ml of 0.01 M $CaCl_2$ for 5 minutes (Rayment and Higginson 1992), the mixture was then filtered and the clear extract was used for B analysis. All elements were analysed either by ICP-OES or ICP-MS.

2.5 Statistical Analysis

Analysis of variance using GLM procedure, and Duncan Multiple Range Test (DMRT) were used to determine significant differences among treatments, using a probability level of $P<0.05$.

2.6 Supplementary data

To further assess how the mode of application of ash influenced B uptake, we used data collected in an earlier study that evaluated growth and yield of canola grown on two soils amended with variable rates of an alkaline fly ash (Yunusa *et al*. 2008). Canola was grown on cores (15 cm ID, 30 cm length) of loamy and sandy soils treated with an alkaline fly ash at rates of 0, 5, 25, 125 or 625 Mg/ha that was incorporated into the top 50 mm layer. Plants were harvested at maturity, and stems and seed weights were determined after oven drying at 60^{o}C for 72 hours. Leaf, stem and seed samples were digested and analysed for B concentration as described by Yunusa et al (2008).

3. RESULTS

3.1. Basic chemical properties of the fly ashes

The fly ashes showed considerable variation in a number of chemical properties (Table 1). Their total carbon content ranged from 0.1 % to 5.5 % while Colwell extractable P ranged from 12 to 222 mg/kg. Furthermore, fly ash $pH_{(H2O)}$ ranged from 3.14 to 10.77, with the FA 1 being the most acidic and the FA11 the most alkaline. The electrical conductivity (EC) in 1: 5 ash : water (w/v) extracts was also extremely variable (0.14 to 19.1 dS/m^{-}) with fly ashes derived from burning brown coal exceptionally saline, due to their high level of soluble cations such as Na, K , Ca and Mg (Table 1).

Total B in the ashes ranged between 12 and 126 mg/kg while B_s ranged from 3.1 to 6.8 mg /kg. Strongly acidic fly ashes (pH< 4.5) had lower total B (<30 mg/kg) with the median value of 19

mg/kg compared with alkaline fly ashes (pH>8) which had total B >60 mg/kg with the median value of 123 mg/kg^{-}. However, the B_s was less than 15 mg/kg for all ashes, with the median values of 5.4 mg/kg. Hot water soluble B as a percentage of total B varied from 5 to 10 % in the alkaline fly ashes and from 17-30 % in the acidic fly ashes, indicating a relatively high B solubility in the acidic fly ashes.

3.2. Soil pH and EC

Both fly ash type and application rate had variable effects on soil pH. In the Belanglo soil, FA 9 significantly ($P<0.05$) increased soil pH by up to 2 pH units at the ash addition rate of 108 Mg/ha (Fig 1a). This could be due to the higher calcium carbonate equivalent (CCE) value of this ash, given its high contents of alkaline elements such as Ca and Mg (Table 1) presumably in oxides and/or carbonate forms (Adriano *et al.* 1980*)*. Other ashes, with very low CCE values (<1 %) did not significantly affect the soil pH; however, there was a small but consistent pH increase at the ash application rate of 12 Mg/ha regardless of the initial pH values of the ashes concerned (Fig 1a). All four fly ashes increased soil EC, mainly in the 0-10 cm depth (Fig 1b) in the Belanglo soil, where EC rose to between 0.207 (±0.089 SE) dS/m and 0.565 (±0.105 SE) dS/m from a background of 0.081 (±0.004 SE) dS/m.

3.3. Crop growth and seed yield

Dry matter production and seed yield were not significantly different ($P>0.05$) among treatments, including the control treatments (Table 3). Variability within the treatments was quite large, due the powdery mildew attack on plants starting from flowering. Despite this,

264 there was a general increase in above-ground dry matter (DM) and seed production by as much
265 as 25 % and 45 % compared with control, in Belanglo and Kangaloon soils respectively. In
266 contrast yield was decreased in the clayey Menangle soil that had poorer drainage.
267
268 *3.4. B uptake and concentration in plant tissues*
269
270 Soils used in this experiment were inherently low in B_s, which resulted in low shoot B contents
271 of 7.2 (±1.84 SE), 6.54 (±30 SE) and 9.4 (±0.32 SE) mg/kg from the unamended Belanglo,
272 Menangle and Kangaloon soils respectively. We observed no B deficiency or toxicity
273 symptoms in any of the canola plants, either in the controls or in any of the ash-treated soils.
274 Shoot B concentration were not significantly (*P=0.05*) affected by ash type or rate of ash
275 additions except with FA 11, which increased the shoot B concentration nearly 2-fold in all
276 three soils compared with respective control soils with the application rate of 108 Mg/ha
277 compared with the unamended control.
278
279 Concentration of B in the shoot and seed did not exceed 20 mg/kg irrespective of fly ash
280 treatments. However, at harvest only a few leaves were left on the plants, and therefore,
281 measured 'shoot B' was primarily stem B rather than "stem-plus-leaf B". Consequently the
282 actual B accumulation in canola plants may have been underestimated in this case. In order to
283 correct this estimate, we used the leaf/stem B concentration ratio of 5, and stem/leaf ratio of 3.2
284 based on the study of Yunusa *et al* (2008) to calculate the leaf B concentration and leaf B
285 uptake in our current study. Based on this, an estimated maximum leaf B concentration was
286 approximately 100 mg/kg was calculated, which, however, is still below the reported toxicity
287 limit of 170 mg/kg (Huett *et al*. 1997), suggesting that fly ash-derived B was unlikely to have

had any adverse effect on canola growth. Concentrations of B in the seeds ranged from 11 - 13 mg/kg in the unamended soils. Fly ash application did not significantly (*P=0.05*) affect the seed B concentration regardless of soil type or ash type. However, on Kangaloon soil, which had the highest initial soil B_s concentration, application of alkaline fly ashes (FA 9, FA 11) (which had higher B_s) increased the seed B by up to 45 % compared with control (Fig 5).

Ash type and rate of application had variable effects on B uptake as a percent of applied B. In general in all soil types application of acidic FA 2 increased percent plant B uptake compared with other ash types although this ash had the lowest soluble B content among all ashes studied. Increasing rates of ash application generally decreased the percent plant B uptake in all soil and ash types (Table 6).

3.5. pH, EC and B concentrations in the leachate

The effects of the various ash treatments on leachate pH and EC were modest (Figs 2 , 3) and there was no noticeable effect on leachate B concentration. The pH of leachate for the control soil was initially (6 weeks after establishment) 3.38 ± 0.2 SE, 5.02 ± 0.59 and 5.55 ± 0.1 SE in the Kangaloon, Menangle and Belanglo soils respectively. In all treatments pH slightly increased (data not shown) with each successive leachate collection, possibly due to a reduction in salt content in the soil. Based on the potential acid neutralization value of the ashes (Table 1), the FA 9 had some inhibitory effect on the beginning of acid neutralization, however, and delayed the pH increase by about 4 weeks (data not shown). The initial (at ~6 weeks after establishment) leachate EC of the control treatments were 0.086 (±0.01SE), 0.112 (±0.01 SE), 17.5 (± 2.90 SE) dS/m for Menangle, Belanglo and Kangaloon soils respectively.

312 FA 9 substantially increased the leachate EC (Fig 3) compared with other ashes in all soils
313 compared with control, but when this ash was applied at the highest rate to the Kangaloon soil
314 it reduced the EC values of the soil leachate.
315
316
317 *3.6. Boron distribution in the soil*
318
319 In the Belanglo soil the concentration of B_t was elevated in the surface 0-10 cm of the soil only
320 when ash was applied at 108 Mg/ha, from the background levels of 3.37 mg/kg to 9.9 and 18.8
321 mg/ kg in the FA 11 and FA 9 ash treatments respectively (Fig 4). Concentrations of B below
322 the layer of ash incorporation were not significantly (*P=0.05*) affected by fly ash treatment.
323
324 *3.7. Supplementary data*
325
326 Fly ash application increased B uptake on the sandy soil more than that observed in the clay soil (Table
327 7). The percentage of ash-derived B taken up by canola decreased with increasing rate of ash
328 application, and was generally less than 1% when ash addition rose to 125 Mg/ha or higher in these
329 high pH soils. Also, plant growth was reduced only when ash applied at 625 Mg/ha, and was increased
330 at ash rates of either 5 or 25 Mg/ha.
331
332 **DISCUSSION**
333
334 Data from both the main and supplementary studies showed that B phytotoxicity was not
335 manifest, and growth not significantly reduced, for canola grown on soil supplied with most of
336 the fly ashes tested. This was despite the ashes differing widely in their basic chemical

characteristics, such as pH, EC and in concentrations of B and cations. Therefore most of the rates of fly ash used in the current study were not large enough to cause B phytotoxicity to canola, or that this plant species is tolerant of high levels of B in the soil. Uptake of B by canola was less than 20 % (Table 6) the amount of this nutrient supplied through the ash when rates of fly ash exceeded 108 Mg/ha. It is most likely however, that the relatively low B contents of the ashes, along with the modest rates at which they were applied, and then only to the top layer of the soil, were important factors in this outcome.

Despite the differences between acidic and alkaline fly ashes in their total B contents, the concentration of B_s in the ash was below 15 mg/kg for all ashes (Table 1). Hot water soluble B is a useful index for determining the potential for B phytotoxicity since their total B contents may not always be a precise indicator for bioavailability of B. All eleven Australian fly ashes studied had B_s less than 15 mg/kg with the median value of 5.4 mg/kg, which is well below the current guideline level of 60 mg/kg set by EPA-NSW These results are consistent with those found by Aitken *et al*. (1984) that Australian fly ashes have relatively low B when compared with those produced overseas in which B levels can be as high as 947 mg/kg and the median value of 266 mg/kg (Moreno *et al*. 2005; James 1982).

In general, there was no significant yield reduction in canola supplied with fly ash at rates that do not exceed 36 Mg/ha in the Belanglo and Kangaloon soils (Tables 3 and 7). This is an encouraging result. The high incidence of fungal attack under the very humid conditions could have constrained any possible yield increases from fly ash treatment, especially at low rates of addition. Yield data for the supplementary study in the preceding year found statistically significant improvement of up to 25% mainly due to higher P uptake by plants supplied with

361 fly ash applied at not more than 25 Mg/ha (Yunusa *et al*. 2008). Reductions in plant growth,
362 particularly in the Menangle soil, with high rates of ash application could not be due to fly ash
363 induced nutrient deficiencies, especially Mg and Mn as reported in some previous studies
364 (Adriano *et al*. 1980). We found no differences in the uptake of any of the essential nutrients
365 (data not shown) by plants grown with fly ash compared with the control treatment suggesting
366 yield reduction was not associated with any nutrient deficiency. Rather soil physical conditions
367 may have adversely affected plant growth particularly in the clayey Menangle soil that was
368 prone to water-logging and surface crusting during the study. In general, regardless of soil type
369 and rate of ash application, FA 9 tended to adversely affect plant growth. This could possibly
370 due to the high salinity of this fly ash, rather than its B concentration, since in none of the ash
371 treatments did the B content of plant shoots reach the phytotoxic threshold of 170 mg/kg
372 (Huett *et al*. 1997). Absence of B phytotoxicity in canola could be due to the ash being applied
373 only to the top layers of the soil from which the roots escaped as the seasons progressed
374 (Yunusa *et al*. 2008).
375
376 Yunusa *et al*. (2008) reported that mixing fly ash at 500 Mg/ha into the whole soil in a 30 cm
377 deep core decreased plant growth, but when the same amount of ash was mixed into the top
378 profile up to 15 cm depth, plant growth was not adversely affected and actually increased. This
379 observation was also consistent with an absence of B phytotoxicity reported for crops supplied
380 with fly ash in the field (Cline *et al*. 2000, Pathan *et al*. 2003). Our method differs from most
381 of the earlier studies in which the whole soil profile was treated with fly ash as is often the
382 case in most studies using limited quantities of soil collected in pots (Kukier *et al*. 1996;
383 Aitken and Bell 1985). In addition, it was also possible that canola was tolerant of soils with
384 high concentration of B, because its roots have an ability to restrict uptake of this element

385 (Kaur *et al*. 2006).

386

387 Although alkaline fly ashes had high B_t content compared with acidic fly ashes, the % B_s was
388 lower in the alkaline fly ashes than in the acidic fly ashes. There was no significant correlation
389 between B_s and B_t (Table 4). The B_s as a percentage of total B (% B_s) ranged from 5- 30 % and
390 these values are within the range reported for widely varying fly ashes from US- approximately
391 50 % (Cox *et al*. 1978), 11-39 % (Pougnet *et al*. 1990) and 17 – 64 % (James *et al*. 1982).
392 Boron solubility in fly ashes depends on several factors including total B content, leachate pH,
393 cation content and ash : water ratio (El-Mogazi *et al*. 1988; Kukier and Sumner 1996; Jankowski *et*
394 *al*. 2006). However, a significant correlation (R^2=0.68**, n=11, *P<0.05*) we found between ash pH and
395 % B_s suggested that pH of fly ash is an important determinant of B solubility, consistent with a study
396 by Kukier and Sumner (1996) in which release of B from fly ash increased with acidification
397 of the extracting solution. They concluded that pH may not directly influence solubility of fly
398 ash B, but rather it promotes the dissolution of fly ash particles, releasing B during the process.
399 If this was the case in our current study a concurrent increase in soluble Si in the soil solution
400 would be expected in parallel with that of B_s but this was not observed (Table 4). Therefore B
401 was not released from the silica matrix and the relationship between pH and B_s reflected the
402 positive correlation between total B content and the inherent pH of the ash. Finally, the positive
403 correlation between water soluble cations and B_s (Table 4) suggested that B_s could be
404 associated with the cationic compounds that become easily plant available if applied to acidic
405 soils.

406

407 The levels of B_s in pure fly ash samples alone may not always accurately estimate potential B
408 phytotoxicity or the B leaching potential when applied to soil. This is mainly due to the

409 substantial changes that occur in the chemical environment of the soil, such as pH (Fig 1),
410 following addition of ash, that could affect solubility, and hence leaching of B from the fly ash.
411 Release of B from fly ash is often greater when ash is applied to acidic soils compared to
412 alkaline soils due to higher solubility of B at lower pHs (Phung *et al*. 1979). Leaching of B
413 from fly ash applied to the soil is an environmental risk especially on sandy soils (Ghodrati *et*
414 *al*. 1995; Ishak *et al*. 2002). Concentration of B in leachate was highly variable, but were all
415 generally below detection limits (<0.05 mg/L, data not presented) as also found in the field
416 (Adriano *et al*. 2002). Changes in soil pH due to addition of fly ash may also affect expression
417 of phytotoxicity due to B or any other elements. Aitken and Bell (1985) found that an alkaline
418 fly ash with a low Bs of 3 μg/g, a level that might be considered non-toxic (Hodgson and
419 Townsend 1973), caused phytotoxicity when applied to an acidic soil. These studies suggest
420 that fly ash B_s value may not be always indicative of the potential B release into the amended
421 soil and continuous monitoring of the B_s in the amended soil will ensure the successful use of
422 fly ash in agricultural soils.
423
424 Fly ash application had variable effect on leachate pH depending on ash type, soil type and the
425 rate of application (Fig 2). The contrasting results with the two alkaline ashes could be
426 associated with their alkaline oxide concentrations. While FA 9 ash with high alkaline oxide
427 content increased leachate pH, FA 11 ash, although alkaline, did not increase the pH possibly
428 due to very low alkaline oxide content. Interestingly, acidic FA 2 ash raised pH of the leachate
429 only at low rates of addition, that is, at rates less than 12 Mg/ha compared with control. This
430 acidic ash that had virtually no liming value increased the pH possibly due the dissolution of
431 silicate minerals and associated proton consumption. Alternatively, release of basic cations
432 from silica matrix and subsequent cation hydrolysis could explain the rise in pH. Fly ash

application rate of up to 36 Mg/ha did not increase the leachate EC values to plant toxic level in any of the soil or ash treatments except FA9 ash which substantially increase the leachate EC (Fig 3) only at the application rate of 108 Mg/ha in the Belanglo soil. Kangaloon soil had extremely high EC values even in the control treatment possibly due to high levels of salt deposit in the subsurface soil layers as this paddock was closer to a swamp. Interestingly application of fly ash slightly reduced leachate EC values in this particular soil, possibly due to soluble salt precipitation by excess soluble cations in the fly ash and need to be further investigated.

3.8. Concluding remarks

We have shown in this study that applying fly ash to the top layers of a soil profile at modest rates limited the expression of B phytotoxicity in canola. Plants were able to escape much of the initial deleterious influence of excessive concentrations of B, and/or any other trace nutrients, once the roots extend beyond the zone into which the ash was incorporated into the soil. The only exception was with the strongly alkaline ash produced from brown coal and whose extreme salinity, rather than its B content *per se*, was the main cause of reduced plant growth. There was generally therefore no expression of phytotoxicity associated with excessive B concentration in ash-treated soils even when fly ash was applied at rate of 108 Mg/ha. This is in contrast to many glasshouse studies in which fly ash was mixed with the entire soil, used containers of limited volumes, often under non-leaching conditions. Under such conditions increased B phytotoxicity is generally observed. However, continued use of fly ash over the long term may result in the build up of B in the top soil layer to which the ash is applied. This could be accentuated further by the return of much of the plant extracted B to the soil through

litter fall. Furthermore, fly ashes having high initial B_t content could increase soil B_t concentration in the top 0-10 cm of the soil, especially when ash is applied at the high rates that exceed 100 Mg/ha. This is in contrast to the expectation that fly ash-derived B may not accumulate in the soils due to leaching because of its high solubility. Some of the fly ash treatments increased soil pH in the treated layer (0-10 cm) presumably because of the dissolution of basic Ca compounds and/or silicate mineral in the ash. We conclude that fly ash can be beneficial to B demanding crops, such as canola, when applied to top soil layers at agronomically realistic rates not exceeding 25 Mg/ha. We expect optimum rates not to exceed 12 Mg/ha and this will be explored in further field studies.

Acknowledgements

We acknowledge with appreciation the assistance with laboratory procedures and facilities from Ms. Narelle Richardson and Gemma Armstrong, and thank Mr. Nawash Haddad, Mr. Aining Mao and Mr Ibby Yunusa for their help with the intact soil core collection and soil and plant sample processing. We express our gratitude to A/Prof. Damian Gore and Mr. Russell Field at Macquarie University for assisting with microwave digestion of sample, and also to Mr. Jim Keegan at the Department of Chemistry, University of Technology Sydney, for his help with the ICP-MS analysis. We acknowledge funding provided by the Ash Development Association of Australia and the Australian Research Council.

References:

Adriano DC, Page AL, Elseewi AA, Chang AC, Straughan I (1980) Utilization and disposal of

fly ash and other coal residues in terrestrial ecosystems: a review. *J. Environ. Qual. ; Vol/Issue: 9:3*, Pages: 333-344.

Adriano DC, Weber J, Bolan NS, Paramasivam S, Koo BJ, Sajwan KS (2002) Effects of high rates of coal fly ash on soil, turfgrass, and groundwater quality. *Water Air and Soil Pollution* **139**, 365-385.

Aitken RL, Bell LC (1985) Plant uptake and phytotoxicity of boron in Australian fly ashes. *Plant and Soil* **84**, 245-257.

Aitken RL, Campbell DJ, Bell LC (1984) Properties of Australian Fly Ashes Relevant to Their Agronomic Utilization. *Australian Journal of Soil Research* **22**, 443-453.

Ashraf M, McNeilly T (2004) Salinity tolerance in Brassica oilseeds. *Critical Reviews in Plant Sciences* **23**, 157-174.

Carlson CL, Adriano DC (1993) Environmental Impacts of Coal Combustion Residues. *Journal of Environmental Quality* **22**, 227-247.

Clark RB, Ritchey KD, Baligar VC (2001) Benefits and constraints for use of FGD products on agricultural land. *Fuel* **80**, 821-828.

Cline JA, Bill M, Torrenueva A (2000) Coal fly ash as a soil conditioner for field crops in southern Ontario. *Journal of Environmental Quality* **29**, 1982-1989.

Colwell JD (1965) An automated procedure for the determination of phosphorus in sodium hydrogen carbonate extract of soil. . *Chemistry and Industry* **10**, 893-895.

Cox JA, Lundquist GL, Przyjazny A, Schmulbach CD (1978) Leaching of boron from coal ash. *Environmental Science & Technology* **12**, 722-723.

Dreesen DR, Gladney ES, Owens JW, Perkins BL, Wienke CL, Wangen LE (1977) Comparison of levels of trace elements extracted from fly ash and levels found in effluent waters from a coal-fired power plant. *Environmental Science & Technology* **11**, 1017-1019.

Elmogazi D, Lisk DJ, Weinstein LH (1988) A Review of Physical, Chemical, and Biological Properties of Fly-Ash and Effects on Agricultural Ecosystems. *Science of the Total Environment* **74**, 1-37.

Ghodrati M, Sims JT, Vasilas BL (1995) Evaluation of Fly-Ash as a Soil Amendment for the Atlantic Coastal-Plain .1. Soil Hydraulic-Properties and Elemental Leaching. *Water Air and Soil Pollution* **81**, 349-361.

529 Hodgson DR, Townsend WN (1973) The amelioration and revegetation of pulverized fuel ash.
530 In 'Ecology and reclamation of devasted land'. (Eds RJ Hutnik, G Davis) pp. 247-270. (Gordon
531 and Breach: London).
532
533 Hollis JF, Keren R, Gal M (1988) Boron Release and Sorption by Fly-Ash as Affected by pH
534 and Particle-Size. *Journal of Environmental Quality* **17**, 181-184.
535
536 Huett DO, Maier NA, Sparrow LA, Piggott TJ (1997) Vegetable Crops. In 'Plant Analysis: An
537 Interpretation Manual'. (Eds DJ Reuter, JB Robinson) pp. 383-464. (CSIRO: Australia).
538
539 Ishak CF, Seaman JC, Miller WP, Sumner M (2002) Contaminant mobility in soils amended
540 with fly ash and flue-gas gypsum: Intact soil cores and repacked columns. *Water Air and Soil*
541 *Pollution* **134**, 287-305.
542
543
544 James WD, Graham CC, Glascock MD, Hanna ASG (1982) Water-Leachable Boron from Coal
545 Ashes. *Environmental Science & Technology* **16**, 195-197.
546
547 Jankowski J, Ward CR, French D, Groves S (2006) Mobility of trace elements from selected
548 Australian fly ashes and its potential impact on aquatic ecosystems. *Fuel* **85**, 243-256.
549
550 Kaur S, Nicolas ME, Ford R, Norton RM, Taylor PWJ (2006) Physiological mechanisms of
551 tolerance to high boron concentration in Brassica rapa. *Functional Plant Biology* **33**, 973-980.
552
553 Keren R, Bingham FT (1985) Boron in Water, Soils, and Plants. *Advances in Soil Science* **1**,
554 230-276.
555
556 Kukier U, Sumner ME (1996) Boron availability to plants from coal combustion by-products.
557 *Water Air and Soil Pollution* **87**, 93-110.
558
559 Kukier U, Sumner ME, Miller WP (1994) Boron Release from Fly-Ash and Its Uptake by
560 Corn. *Journal of Environmental Quality* **23**, 596-603.
561
562
563 McDowell LR (1992) 'Minerals in animal and human nutrition.' (Academic Press Inc:
564 Toronto).
565
566 Moreno N, Querol X, Andres JM, Stanton K, Towler M, Nugteren H, Janssen-Jurkovicova M,
567 Jones R (2005) Physico-chemical characteristics of European pulverized coal combustion fly
568 ashes. *Fuel* **84**, 1351-1363.
569
570 Murphy J, Riley JP (1962) A modified single solution method for the determination of
571 phosphorus in natural waters. *Analitica Chemica acta* **27**, 31-36.
572
573
574 Olsen SR, Cole CV, Watanabe FS, Dean LA (1954) Estimation of available phosphorus in
575 soils by extraction with sodium bicarbonate. *USDA* **Cir No. 939**.

Pathan SM, Aylmore LAG, Colmer TD (2003) Soil properties and turf growth on a sandy soil amended with fly ash. *Plant and Soil* **256**, 103-114.

Phung HT, Lam HV, Page AL, Lund LJ (1979) The practice of leaching boron and soluble salts from fly ash-amended soils. *Water, Air, and Soil Pollution* **12**, 247-254.

Plank CO, Martens DC (1974) Boron availability as influenced by application of fly ash to soil. *Soil Science Society of America Proceedings* **38**, 974-.

Pougnet MAB, Wyrleybirch JM, Orren MJ (1990) The Boron and Lithium Content of South-African Coals and Coal Ashes. *International Journal of Environmental Analytical Chemistry* **38**, 539-549.

Rayment G, Higginson F (1992) Australian Laboratory Handbook of Soil and Water Chemical Methods.

Sims JT, Vasilas BL, Ghodrati M (1995) Evaluation of Fly-Ash as a Soil Amendment for the Atlantic Coastal-Plain .2. Soil Chemical-Properties and Crop Growth. *Water Air and Soil Pollution* **81**, 363-372.

Tolle DA, Arthur MF, Van Voris P (1983) Microcosm/field comparison of trace element uptake in crops grown in fly ash-amended soil. *The Science of the Total Environment* **31**, 243-261.

Yunusa IAM, Eamus D, DeSilva DL, Murray BR, Burchett MD, Skilbeck GC, Heidrich C (2006) Fly-ash: An exploitable resource for management of Australian agricultural soils. *Fuel* **85**, 2337-2344.

Yunusa IAM, Manoharan V, DeSilva DL, Eamus D, Murray BR, Nissanka SP (2008) Physiology, yield and elemental accumulation in canola (Brassica napus) grown on soil amended with coal fly-ash. *Journal of Environmental Quality* **in print**.

619

620 **Figure legend**

621

622 Fig 1. Effect of fly ash application on (a) soil pH (b) soil EC at the surface 0-10 cm of the soil
623 profile(vertical bar=standard error).

624 .

625 Fig 2. Effect of fly ash application (a) leachate pH. (vertical bar=standard error).
626 (average across 4^{th} to 7^{th} leachates)

627

628 Fig 3. Effect of fly ash application (a) leachate EC. (vertical bar=standard error).
629 (average across 4^{th} to 7^{th} leachates)

630

631 Fig 4. Effect of fly ash application on B distribution in the soil profile (vertical bar=standard
632 error)

Table 1. Selected chemical characteristics of the Australian fly ashes in terms of their pH, electrical conductivity (EC), and concentrations of total and soluble boron and selected water soluble cations and soluble Si

Ash source	pH	EC	% CCE[a]	B_t[b]	Na[c]	K[c]	Ca[c]	Mg[c]	Si[c]	B_s[d]	Extractable-P[e]
		dS/m		←				mg/kg			→
FA 1	3.14	0.91	0.00	30	145	110	301	42	48	9.1	12.89
FA 2	3.28	1.10	0.10	12	192	52	616	82	125	3.1	222.4
FA 3	3.83	0.22	0.00	19	54	10	9	5	14	3.4	7.8
FA 4	3.96	0.14	0.00	18	41	12	9	4	17	3.2	3.1
FA 5	4.36	0.23	0.00	37	25	49	73	7	10	6.9	10.3
FA 6	5.86	0.47	0.10	24	106	12	465	23	26	5.4	6.5
FA 7	5.91	0.15	0.19	49	71	4	80	29	19	2.5	5.9
FA 8	8.78	18.48	0.00	136	16000	1482	7521	15428	17	13.7	19.4
FA 9	9.04	19.06	2.43	127	18020	1365	7647	16060	17	6.8	12.6
FA 10	10.68	0.70	1.53	120	269	6	793	5	33	5.4	436.2
FA11	10.77	0.54	0.66	66	74	34	766	5	23	6.7	58.7

[a]Calcium carbonate equivalent; [b]Total concentrated HNO_3 leachable B; [c]Water soluble cations and Si (1:6 soil : water); [d]Hot 0.01 M $CaCl_2$ extractable B [e]Colwel extractable P

Table 2. Selected chemical properties of Belanglo, Kangaloon and Menangle soils.

Soil location	Soil order	pH (1: 5 soil:water)	EC (1: 5 soil: water)	Cation Exchange Capacity	Total organic Carbon	Total B	Hot water soluble B	Colwel Extractable P
			dS/m	cmol (+)/kg	%	mg/kg	mg/kg	mg/kg
Belanglo	Typic kandiaquult	5.02	0.072	3.98	1.78	4.6	0.72	10
Kangaloon	Rhodic hapludox	5.41	0.222	15.78	2.82	9.8	1.65	8
Menangle	Typic paleudult	5.40	0.266	19.53	4.92	18	1.52	199

Table 3. Relative dry matter and seed yield of canola growing on soil amended with a range of coal fly ashes

Soil	Fly ash	Rate of fly ash application (Mg/ha)			
		0	12	36	108
			Relative DM yield/plant		
Belanglo	FA 2	1.00	1.00	1.23	1.11
	FA 4	1.00	1.25	1.22	1.11
	FA 11	1.00	1.04	1.01	1.05
	FA 9	1.00	1.16	0.94	0.38
Menangle	FA 2	1.00	0.86	0.81	0.94
	FA 4	1.00	0.57	0.42	0.79
	FA 11	1.00	0.16	0.82	0.39
	FA 9	1.00	0.94	0.74	0.77
Kangaloon	FA 2	1.00	1.26	1.11	1.45
	FA 4	1.00	1.13	0.90	1.35
	FA 11	1.00	0.77	1.33	0.69
	FA 9	1.00	0.50	0.74	1.03
			Relative seed yield/plant		
Belanglo	FA 2	1.00	0.62	1.05	0.92
	FA 4	1.00	0.96	1.09	1.22
	FA 11	1.00	0.78	0.85	0.86
	FA 9	1.00	0.50	0.43	0.38
Menangle	FA 2	1.00	0.74	0.85	0.86
	FA 4	1.00	0.44	0.50	0.53
	FA 11	1.00		0.50	0.29
	FA 9	1.00	0.77	0.99	0.67
Kangaloon	FA 2	1.00	1.19	1.11	1.48
	FA 4	1.00	1.18	0.73	1.44
	FA 11	1.00	0.72	1.28	0.62
	FA 9	1.00	0.61	0.64	0.69

Table 4. Correlation coefficients between pH, EC, selected water soluble cations, soluble Si, Bt and Bs for 11 Australian fly ashes

	B_t	B_s
Na	0.77**	0.61**
K	0.76**	0.68**
Ca	0.80**	0.65**
Mg	0.76**	0.69**
Si	-0.32	-0.23
B_s	0.59	
pH	0.83**	0.35
EC	0.77**	0.64**

**= statistically significant at $P<0.05$

Table 5. Effect of fly ash application on seed B concentrations (mg/kg).

Soil	Ash	Rate of fly ash application (Mg/ha)			
		0	12	36	108
Belanglo	Control	11.6 (0.39)			
	FA 2		8.7 (0.92)	10.7 (0.09)	11.6 (3.11)
	FA 4		11.1 (3.22)	11.6 (3.42)	9.3 (-)
	FA 11		13.1 (3.22)	8.4 (0.20)	10.6 (2.82)
	FA 9		8.5 (0.36)	8.23 (-)	-
	Control	10.9 (0.20)			
Menangle	FA 2		10.9 (0.03)	8.6 (1.46)	11.9 (1.06)
	FA 4		10.2 (1.21)	22.8 (-)	9.4 (1.73)
	FA 11			-	12.9 (3.40)
	FA 9		9.71 (6.57)	17.6 (3.88)	9.2 (-)
Kangaloon	Control	13.2 (3.08)			
	FA 2		15.9 (2.40)	12.3 (1.92)	11.9 (4.07)
	FA 4		11.5 (4.66)	9.5 (1.36)	19.3 (1.04)
	FA 11		7.7 (0.27)	19.2 (-)	15.9 (3.34)
	FA 9		19.1 (1.49)	16.8 (5.35)	12.5 (1.07)

-data not available; values within brackets are standard error of mean

Table 6. Uptake (mg) and distribution of B in canola in relation to amounts of ash applied B at harvest on three soil types

Ash type	Rate of application of ash (Mg/ha)	Amount of B input (mg/core)	Shoot (Stem + leaf[¥]) uptake of B (mg)	Seed B (mg)	% B uptake[¶]
			Belanglo soil		
Control	0	0	0.31	0.03	-
FA 2	12	0.25	0.31	0.02	132
	36	0.77	0.27	0.04	40
	108	2.29	0.44	0.04	20
FA 4	12	0.38	0.31	0.04	91
	36	1.15	0.22	0.03	21
	108	3.44	0.47	0.03	14
FA 11	12	1.39	0.51	0.04	39
	36	4.22	0.39	0.03	10
	108	12.61	0.61	0.03	5
FA 9	12	2.67	0.33	0.02	13
	36	8.13	0.36	0.01	5
	108	24.26	0.24	-	1
			Menangle soil		
Control	0	0	0.42	0.049	-
FA 2	12	0.25	0.63	0.036	267
	36	0.77	0.50	0.033	69
	108	2.29	0.70	0.046	32
FA 4	12	0.38	0.25	0.016	70
	36	1.15	0.31	0.051	31
	108	3.44	0.41	0.022	12
FA 11	12	1.39	0.07		5

	36	4.22	0.36	0.008	9
	108	12.61	0.38	0.05	3
FA 9	12	2.67	0.57	0.03	23
	36	8.13	0.54	0.08	8
	108	24.26	0.58	0.05	3
			Kangaloon soil		
Control	0	0	0.551	0.06	-
FA 2	12	0.25	0.57	0.08	258
	36	0.77	0.70	0.06	98
	108	2.29	0.47	0.06	22
FA 4	12	0.38	0.53	0.06	154
	36	1.15	0.53	0.03	48
	108	3.44	0.67	0.11	22
FA 11	12	1.39	0.34	0.02	25
	36	4.22	0.78	0.10	21
	108	12.61	0.84	0.04	7
FA 9	12	2.67	0.33	0.05	14
	36	8.13	0.46	0.05	6
	108	24.26	0.42	0.02	2

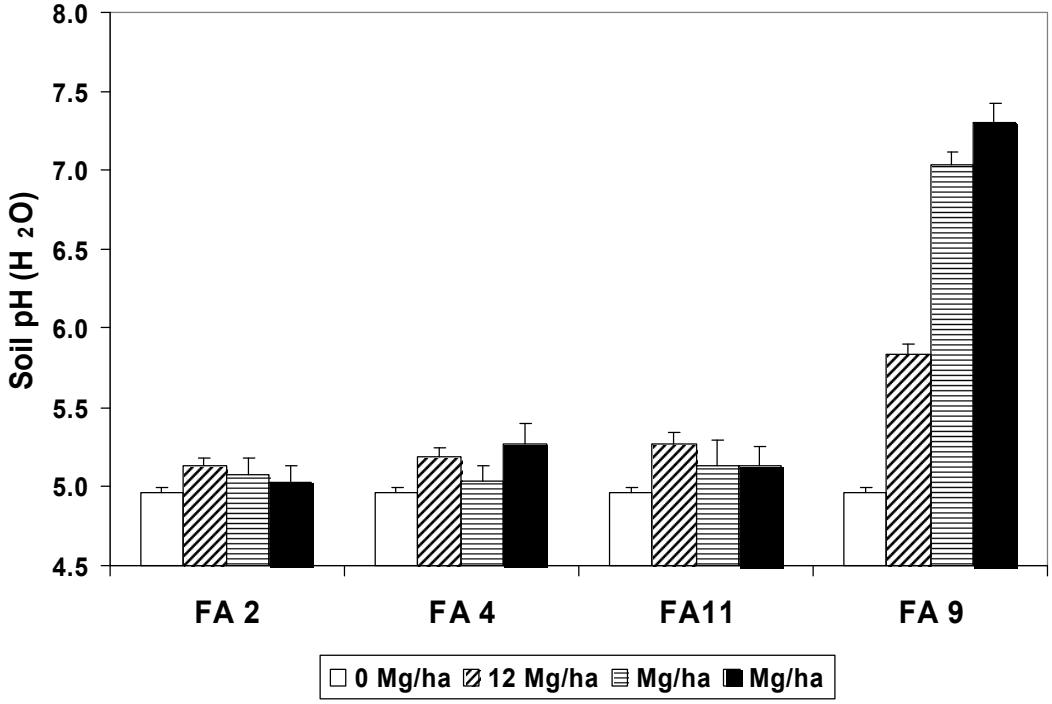
[¥]Leaf weight and leaf B concentration was estimated using data from Yunusa et al (2008); [¶]% uptake = (Amount of B removed by the plant in the ash treated soil/amount of B added through Ash) *100. In this calculation, we assumed that ash derived B was highly soluble and therefore easily absorbed by plants compared with native soil soluble B.

Table 7. Effect of fly ash application method, soil type and rate of addition on B uptake by Canola (mg/plant)

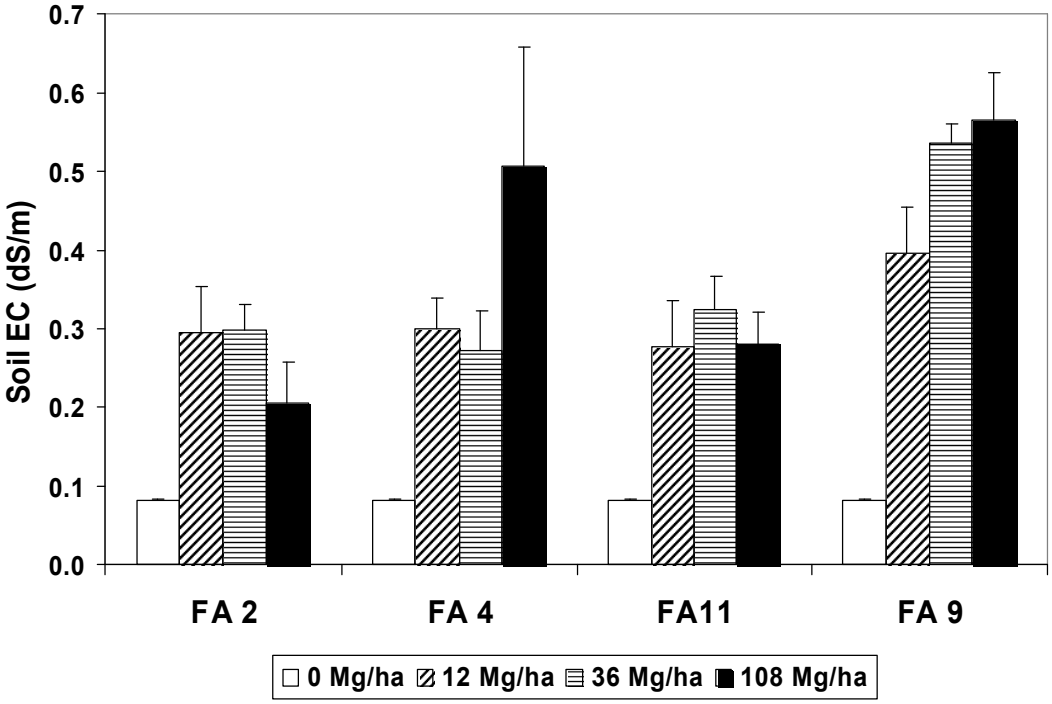
Soil type	Soil pH	Rate of application (Mg/ha)	Amount of B added (mg/core)	Total plant B uptake (mg)	% uptake of B[δ]	Plant dry matter weight (g)/pot[ξ]
Loamy	6.57	0	0	0.126		11.2
		5	0.583	0.099	16.9	14.9
		25	2.92	0.161	5.5	12.3
		125	14.65	0.099	0.7	9.2
		625	72.93	0.088	0.1	5.0
Sand	6.38					
		0	0	0.123		7.9
		5	0.583	0.157	26.9	14.5
		25	2.92	0.144	4.9	9.3
		125	14.65	0.137	0.9	9.0
		625	72.93	0.112	0.2	5.6

[δ](Total B uptake by plant/Ash added B)*100,[ξ] Plant shoot weight at harvest

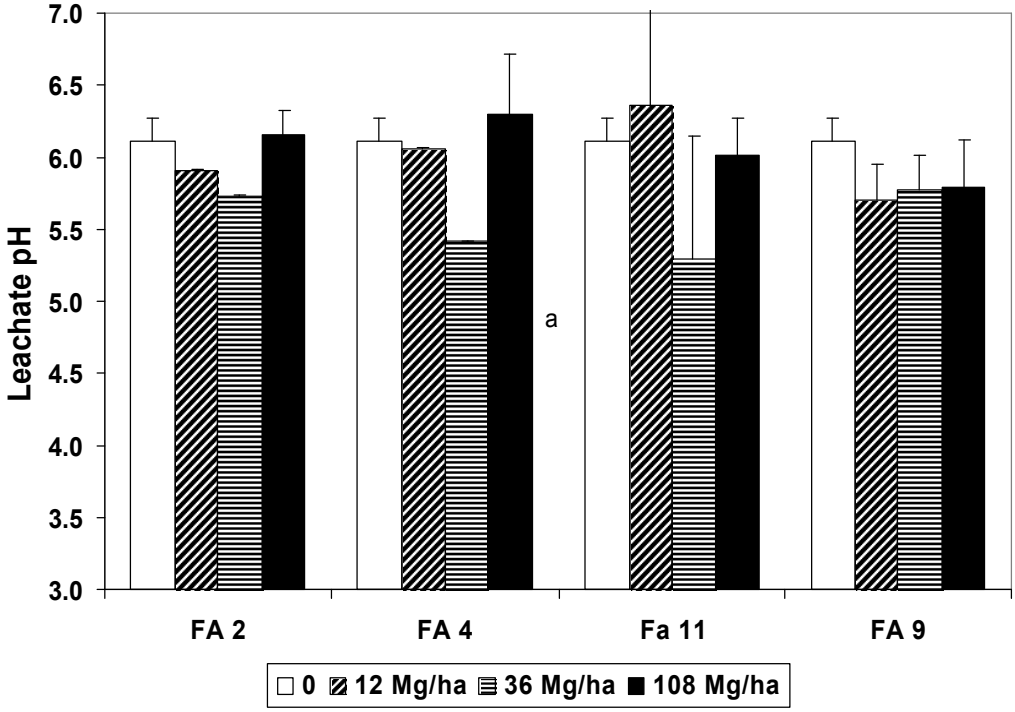
a


8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
Soil pH (H 2O)
FA 2
FA 4
FA11
FA 9
0 Mg/ha
12 Mg/ha
Mg/ha
Mg/ha

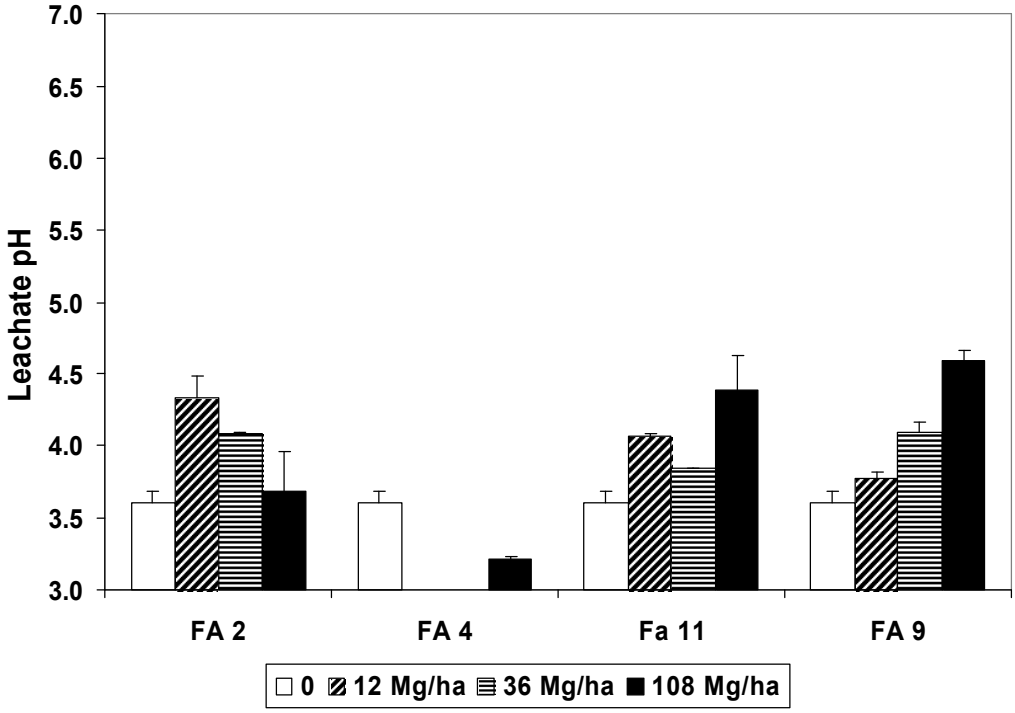
b


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Soil EC (dS/m)
FA 2
FA 4
FA11
FA 9
0 Mg/ha
12 Mg/ha
36 Mg/ha
108 Mg/ha

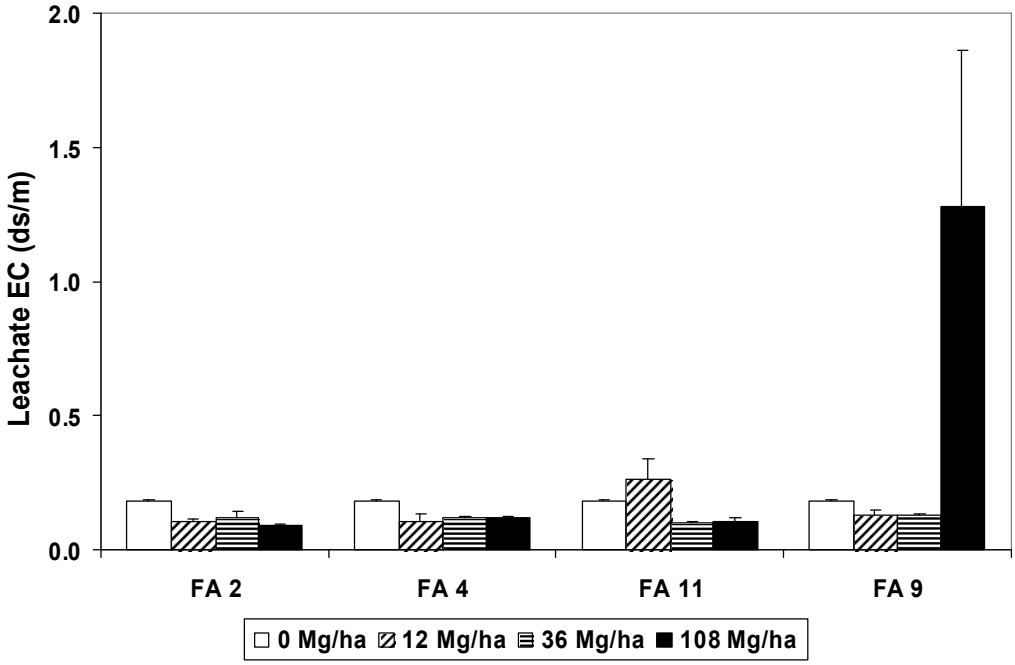
a


7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Leachate pH
a
FA 2
FA 4
Fa 11
FA 9
0
12 Mg/ha
36 Mg/ha
108 Mg/ha

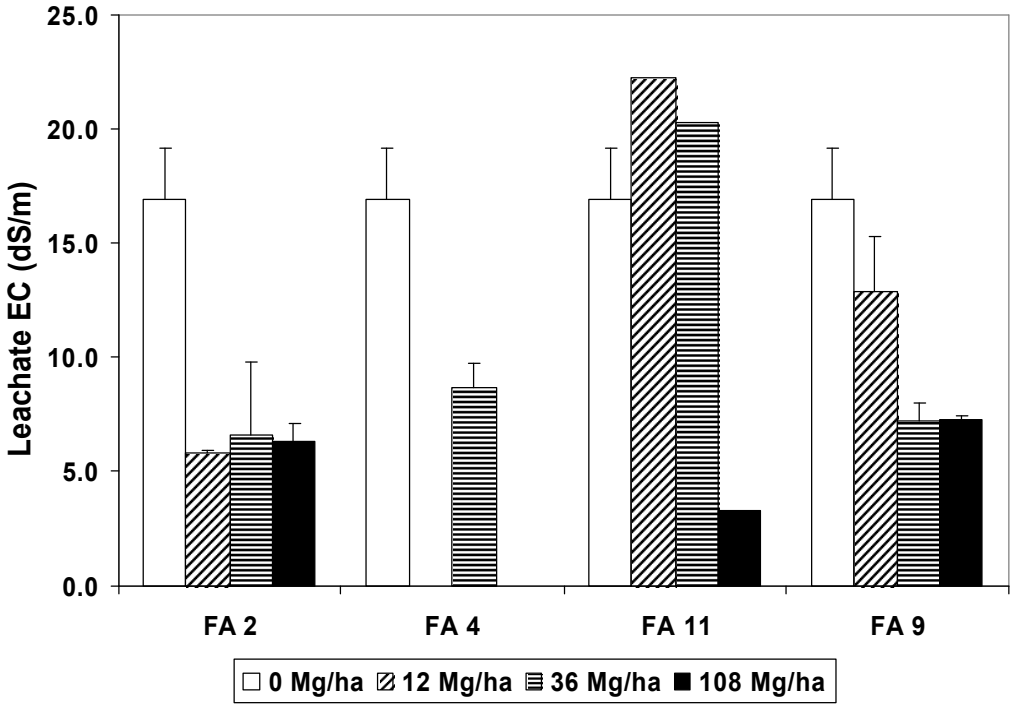
b

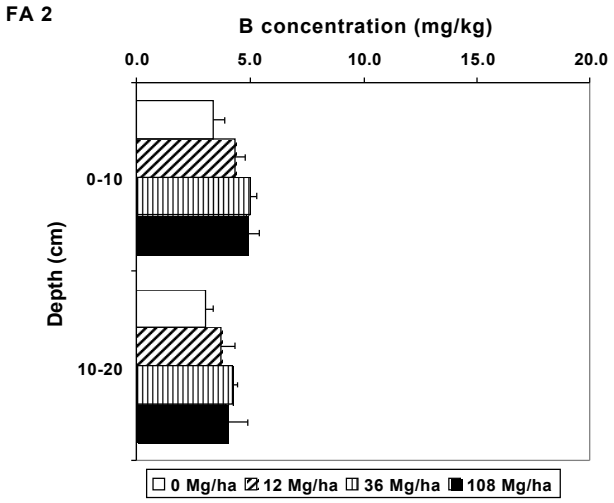

7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
Leachate pH
FA 2
FA 4
Fa 11
FA 9
0
12 Mg/ha
36 Mg/ha
108 Mg/ha

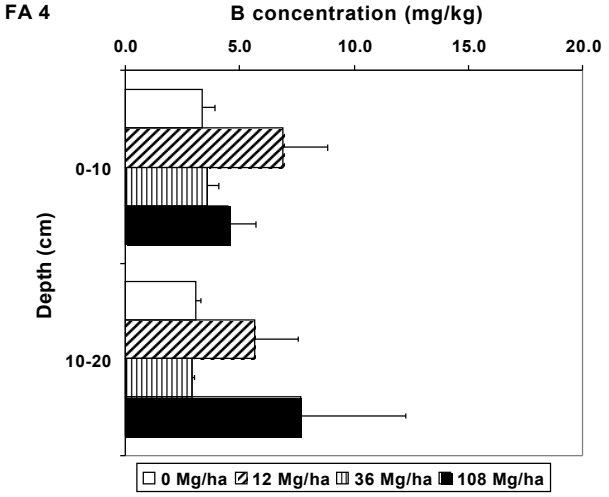
a

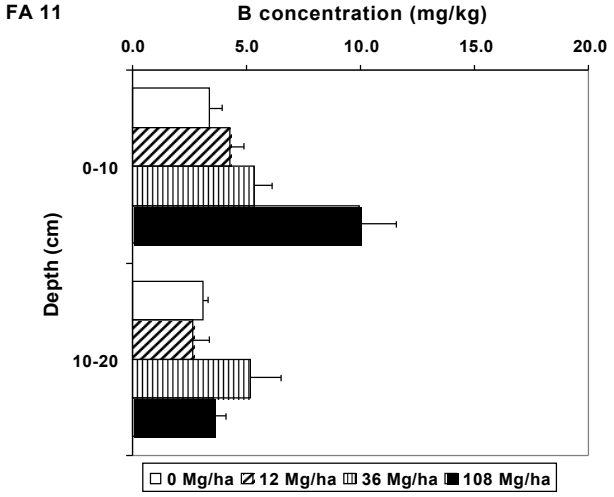

Leachate EC (ds/m)
2.0
1.5
1.0
0.5
0.0
FA 2
FA 4
FA 11
FA 9
0 Mg/ha
12 Mg/ha
36 Mg/ha
108 Mg/ha

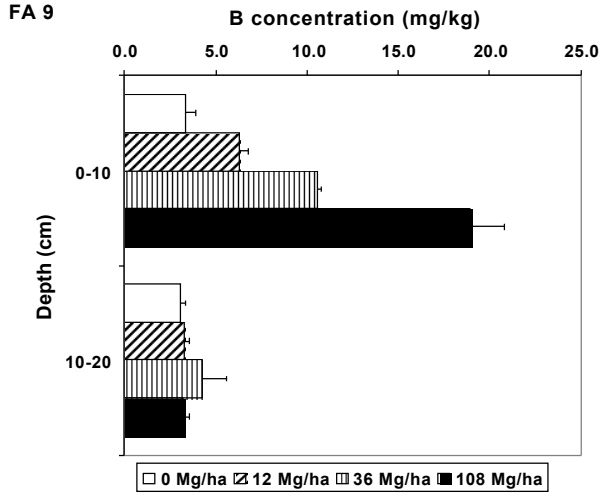
b


Leachate EC (dS/m)
25.0
20.0
15.0
10.0
5.0
0.0
FA 2
FA 4
FA 11
FA 9
0 Mg/ha
12 Mg/ha
36 Mg/ha
108 Mg/ha


FA 2
B concentration (mg/kg)
0.0
5.0
10.0
15.0
20.0
Depth (cm)
0-10
10-20
0 Mg/ha
12 Mg/ha
36 Mg/ha
108 Mg/ha


FA 4
B concentration (mg/kg)
0.0
5.0
10.0
15.0
20.0
Depth (cm)
0-10
10-20
0 Mg/ha
12 Mg/ha
36 Mg/ha
108 Mg/ha


FA 11
B concentration (mg/kg)
0.0
5.0
10.0
15.0
20.0
Depth (cm)
0-10
10-20
0 Mg/ha
12 Mg/ha
36 Mg/ha
108 Mg/ha


FA 9
B concentration (mg/kg)
0.0
5.0
10.0
15.0
20.0
25.0
Depth (cm)
0-10
10-20
0 Mg/ha
12 Mg/ha
36 Mg/ha
108 Mg/ha