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Plant uptake and phytotoxicity of boron in Australian fly ashes

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Summary French bean (*Phaseolus vulgaris* cv. Redland Pioneer) and Rhodes grass (*Chloris gayana* cv. Pioneer) were grown in glasshouse experiments to examine the potential for phytotoxicity of B in a range of Australian fly ashes. In each experiment, the ashes used were either untreated, leached or adjusted to pH 6.5 and subsequently leached.

In the first experiment, the yield and B status of plants grown on five fly ashes mixed (5 and 10% by weight) with an acid-washed sand were measured and, with the exception of one ash, yield differences among ash sources and among ash treatments were attributed to differences in the degree of B toxicity. In a subsequent experiment, a fly ash with properties representative of most Australian ashes was mixed (0, 15, 30, 70 and 100% by weight) with a sandy loam, and the yield and mineral composition of plants grown on these mixtures determined. Although the available water capacity of the soil was substantially increased by fly ash addition, incorporating large proportions of untreated fly ash resulted in poor plant growth primarily due to B toxicity. In both experiments, leaching the ash reduced the potential for B toxicity, whereas adjustment of the pH to 6.5 and subsequent leaching of the fly ash resulted in plants with normal levels of B.

There were marked differences in both the tissue levels of B and the extent of B toxicity symptoms between the two species. Rhodes grass appeared to be able to tolerate higher B contents in the growing medium by taking up much less of the element than French bean. The results indicate that phytotoxicity of B would be a major problem in establishing vegetation on ash dams and in the agronomic utilization of unweathered fly ashes in Australia.

Introduction

Fly ash, the principal by-product of coal-fired power stations, is the residue resulting from the combustion of pulverised fuel. Only a small proportion of the ash produced in Australia is utilized, and commonly the material is piped as a slurry of ash and water to storage ponds located near power stations. A number of studies in North America and Europe have investigated the potential for the agronomic utilization of fly ash[10,11,19,23] and, in Australia, the use of fly ash to improve the water holding capacity of coarse-textured soils[6,24] and as a source of Mg for pastures[15] has been proposed. A possible limitation to the agronomic utilization of fly ash may be the harmful effect on plant growth of certain toxic elements. Potential toxic elements identified in fly ash include Se[4,12], Al[7], As[7] and B[1,8].

Of the potential toxic elements in fly ash, B has been considered as the element most likely to cause phytotoxicity in plants[16,17]. Applications of relatively small amounts of fly ash to soils have resulted in increased B uptake by plants in some studies[12,25], although toxicity levels in plant tissues were not reported. On the other hand, plants grown on untreated ash alone have been shown to exhibit B toxicity[8]. A recent laboratory study of the properties of Australian fly ashes[3] has indicated that B is likely to be one of the major limitations to their agronomic utilization.

To our knowledge, there have been no published data on the B toxicity of Australian fly ashes, and such information is required before their agronomic use can be recommended. The objective of the present investigation, therefore, was to examine the potential for B toxicity to plants in five Australian fly ashes covering a range of coal sources and power station-operating conditions. Uptake and accumulation of B by two species, French bean (*Phaseolus vulgaris*), known to be susceptible to B toxicity[5] and Rhodes grass (*Chloris gayana*), a salt tolerant species[26], were studied in two glasshouse experiments in which the ashes were added to a sand and a sandy loam. To simulate the weathering and subsequent leaching of ash which may occur in ash ponds and to enable differentiation between the effect of B and other chemical factors on plant growth, the effect of adding leached and pH-adjusted and leached fly ash was also studied.

Materials and methods

Bulk samples of freshly precipitated fly ash were collected from power stations at Swanbank (Queensland), Callide (Queensland), Munmorah (New South Wales), Tallawarra (New South Wales) and Port August (South Australia). Important properties of these ashes are given in Table 1. A more detailed characterization of the agronomic properties of these ashes has been given in a previous study[3]. Subsamples of each ash were successively batch-leached (24 h) with deionized water (1:5 ash:water) until the electrical conductivity of the supernatant was < 0.2 mS cm^{-1} and then dried at 40°C. A second series of subsamples were similarly leached except that, for the first wash, dilute H_2SO_4 was added to adjust the pH to 6.5 and the suspension allowed to equilibrate for 48 h. Samples of untreated, leached and pH-adjusted leached ashes were analysed for hot water-soluble boron[27] by inductivity coupled plasma emission spectroscopy.

Experiment 1

This experiment was designed to assess the potential for B toxicity in the five ashes and to make comparisons of B release characteristics of the ashes from uptake data. Each ash was mixed with an acid-washed coarse sand (2.0–0.2 mm) at rates of application of 5% and 10% by weight (the addition of fly ash at rates such as these had been shown to markedly improve the available water capacity of sands[6]). Two test species, French bean (*Phaseolus vulgaris*, cv. Redland Pioneer) and Rhodes grass (*Chloris gayana* cv. Pioneer) were used. The experimental design for each species was a 5 × 3 × 2 × 3 factorial involving five fly ashes each ash either untreated, leached or leached after the pH was adjusted to 6.5, two levels of ash application and three replications.

Two kg of the various mixtures were mixed with a complete application of essential nutrients

Table 1. Properties of the fly ashes sampled from various power stations

Ash	Clay (%) (< 0.002 mm)	Silt (%) (0.002–0.02 mm)	Sand (%) (0.02–2.0 mm)	pH (1:5 in H_2O)	E.C.saturation extract ($mS\ cm^{-1}$)	Gravimetric moisture content (%)		Available water capacity (%)
						10 k Pa	1500 k Pa	
Swanbank (Qld.)	11	52	37	11.7	2.7	64.8	9.3	55.5
Callide (Qld.)	9	6	85	8.9	0.41	44.8	3.6	41.2
Munmorah (N.S.W.)	7	45	48	11.8	4.8	42.8	2.2	40.6
Tallawarra (N.S.W.)	8	51	41	9.8	1.6	83.8	2.9	80.9
Port Augusta (S.A.)	13	54	33	11.3	3.5	29.4	2.4	27.0

in solution form and the mixes placed in polyethylene-lined pots. The nutrient application rates (kg ha^{-1}) of 60, 25, 30, 12, 10, 5, 1, 1, 1 and 0.1 for N, P, K, S, Ca, Mg, Cu, Zn, Mn and Mo respectively were designed to ensure nonlimiting supply of nutrients and were based on chemical tests and experience. Four plants of the respective test species were established in each pot, and the pots watered daily with deionized water to a matric suction of 10 kPa, the moisture contents at 10 kPa and 1500 kPa for each mixture being previously determined using a pressure plate apparatus. Two weeks after sowing, Fe was applied to all plants as a foliar application of 1% Fe sequestrene solution.

Plant tops were harvested 6 weeks after germination, washed in deionized water, dried at 60°C and the dry matter yield recorded. The dried plant material was finely ground, subsamples were digested with concentrated nitric and perchloric acids and the concentrations of Cu, Zn, Fe, Mn, Mo and B in the diluted digest were determined by inductively coupled plasma emission spectroscopy. Following the harvest of plant tops, the potted mixtures were air dried and subsampled; the pH and electrical conductivity of the subsamples were then determined in 1:5 solid : water extracts after shaking for 1 hour.

Experiment 2

The aim of this glasshouse experiment was to assess the plant growth on a sandy loam when mixed with varying proportions of fly ash. Large stocks of this particular soil (which had a pH of 6.0, 12% clay, 6% silt and 82% sand) are used in the city of Brisbane as a top dressing and garden soil. In this experiment, fly ash from Swanbank (Queensland) was used since it had properties representative of most Australian ashes[6]. Swanbank ash, either untreated, leached or leached after the pH was adjusted to 6.5, was mixed with the soil to give proportions of 0, 15, 30, 70 and 100% ash by weight. The same two test species as in Experiment 1 were used; the experimental design for each species was thus a randomized complete block with 13 treatments and 4 replications.

The moisture contents at 0.1, 1.0, 10, 100 and 1500 kPa were determined for each ash : soil mixture using a pressure plate apparatus. Glasshouse and analytical techniques identical to those previously outlined for Experiment 1 were used except that the rates of application (kg ha^{-1}), for N, P, K and S were 200, 200, 100 and 40 respectively. Previous work with the ashes and soil indicated that these levels would produce maximum yields of both test species at any given ash : soil ratio.

Results

Experiment 1

Ash source significantly ($P \leqslant 0.01$) affected the yield of both test species (Figures 1 and 2). Bean yields were in the order: Swanbank = Munmorah = Tallawarra > Pt. Augusta > Callide, whereas Rhodes grass yields were in the order Munmorah = Tallawarra = Pt. Augusta > Swanbank = Callide.

The addition of 10% ash generally resulted in higher bean yields than the 5% ash treatment in the leached and pH-adjusted and leached treatments (Fig. 1). In the untreated ashes, Pt. Augusta was the only ash in which 10% ash addition significantly reduced bean yields compared with the 5% addition. Rhodes grass yields were not significantly affected by ash percentage and, for brevity, only the mean of 5% and 10% ash additions is presented (Fig. 2). As in the case of bean yields, the leached and pH-adjusted and leached treatments generally resulted in higher grass yields than the untreated ash treatments (Figures 1 and 2).

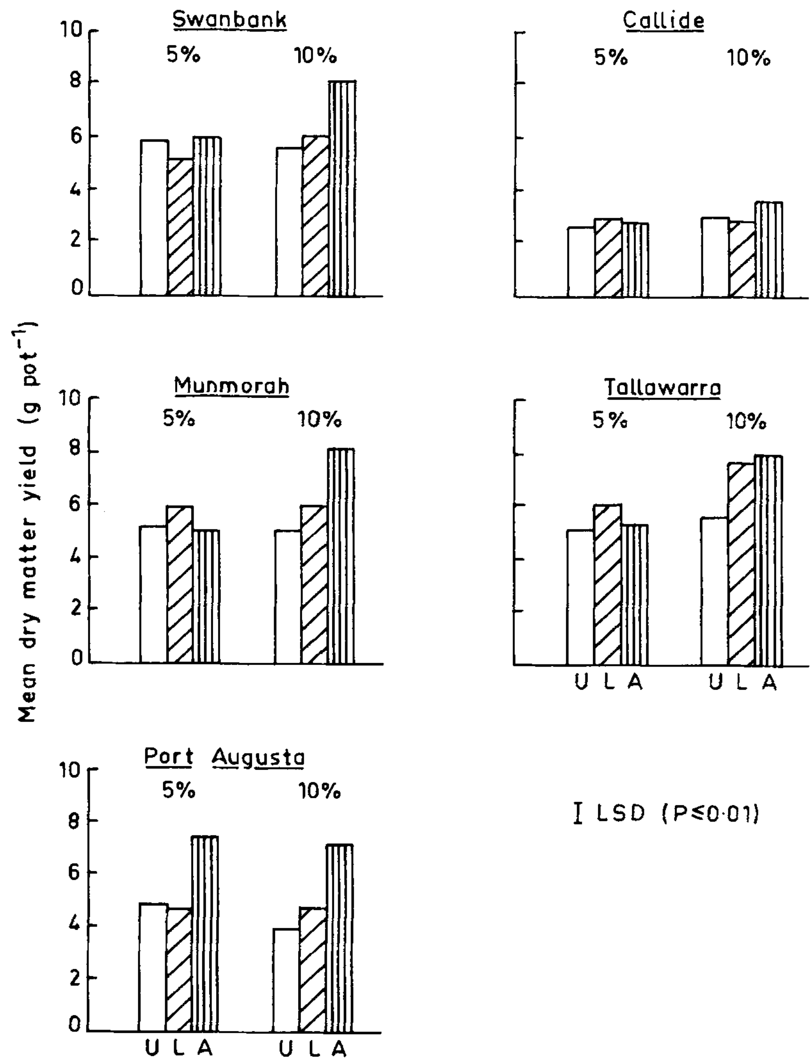

Fig. 1. Dry matter yield of bean tops in *untreated* (U), *leached* (L) and *pH-adjusted and leached* (A) fly ash-sand mixtures.

Tissue concentrations of, and uptake of B by, both bean and Rhodes grass tops were significantly ($P \leqslant 0.01$) affected by ash source, ash treatment and percentage of ash incorporated with the sand (Table 2). For both levels of ash addition and both species, the B concentration and uptake decreased in order untreated ash > leached ash > pH-adjusted and leached ash. Concentration and uptake of B in Rhodes grass was substantially lower than that in bean plants, and this was reflected in the much lower incidence of boron toxicity symptoms with Rhodes grass than with beans. In each species, B toxicity was

Table 2. Mean boron concentration ($\mu g\ g^{-1}$) and uptake ($\mu g\ pot^{-1}$) in tops of bean and Rhodes grass grown in various ash : sand mixtures (Experiment 1)

Ash Source	Treatment†	Hot-water-soluble boron ($\mu g\ g^{-1}$)§	Bean: B conc. 5	Bean: B conc. 10	Bean: B uptake 5	Bean: B uptake 10	Rhodes grass: B conc. 5	Rhodes grass: B conc. 10	Rhodes grass: B uptake 5	Rhodes grass: B uptake 10
			Ash-sand mixture (% ash)				Ash-sand mixture (% ash)			
Swanbank (Qld)	U	3.0	80	131*	469	734	25	35	138	137
	L	2.6	63	100	331	634	21	24	123	129
	A	0.4	26	24	160	199	9	13	49	97
Callide (Qld)	U	3.5	55	63	143	192	14	21	67	121
	L	0.3	31	39	89	116	13	11	70	65
	A	0.3	30	41	84	142	13	15	66	83
Munmorah (N.S.W.)	U	32.9	265*	377*	1502	1919	63	192*	452	1188
	L	7.7	97	151	620	917	36	60	211	348
	A	0.4	32	45	162	373	12	19	90	128
Tallawarra (N.S.W.)	U	27.7	146*	243*	740	1346	68	111	430	819
	L	2.0	49	61	307	464	22	29	133	201
	A	0.9	36	38	154	250	15	20	83	135
Port Augusta (S.A.)	U	25.9	280*	427*	1372	1742	104	130*	641	866
	L	12.2	192*	299*	914	1414	84	85	529	395
	A	47	82	111	609	797	29	35	201	241
LSD ($P \leqslant 0.01$)			63		334		25		169	

† U = untreated, L = leached, A = pH-adjusted and leached.
§ Determined in untreated, leached and pH-adjusted and leached fly ashes prior to mixing with the sand.
* Indicates plants showing boron toxicity symptoms.

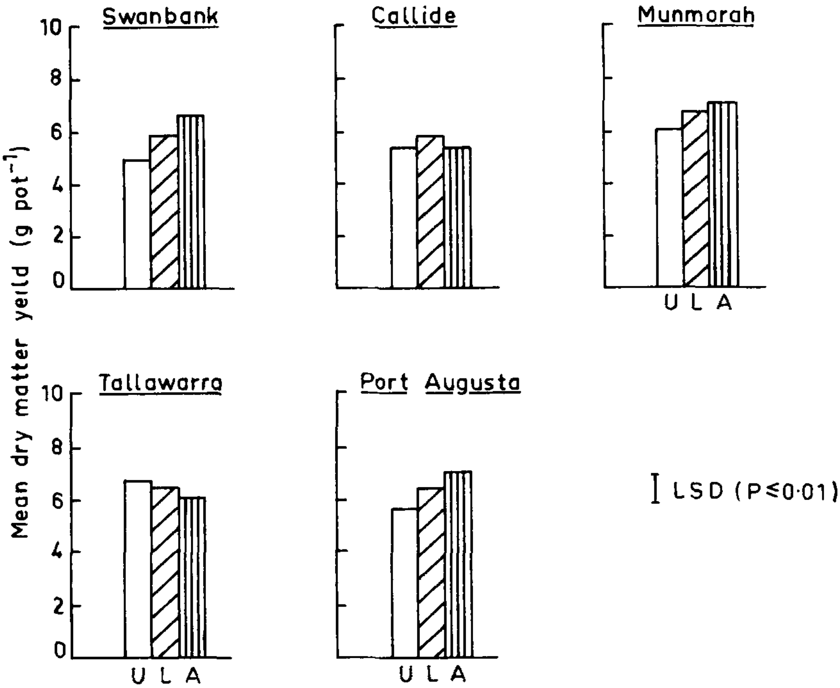

Fig. 2. Mean dry matter yield of Rhodes grass tops in *untreated* (U), *leached* (L) and *pH-adjusted and leached* (A) fly ash-sand mixtures (mean of 5 and 10% ash additions).

Table 3. Mean yield (g pot^{-1}) of, and boron concentration ($\mu g\ g^{-1}$) in, bean and Rhodes grass tops grown in ash : soil mixtures (Experiment 2)

Loam (%)	Ash (%)	pH†	Beans Yield	Beans B conc.	Rhodes grass Yield	Rhodes grass B conc.
100	0	5.7	4.62	88	7.62	33
Untreated						
85	15	7.2	3.64	209*	5.72	78
70	30	7.4	2.69	281*	6.28	114
30	70	7.5	2.39	501*	3.86	158*
0	100	7.9	1.81	543*	0.32	149*
Leached						
85	15	7.3	5.95	157	6.66	54
70	30	7.5	4.94	158	7.34	59
30	70	7.6	3.60	297*	8.43	84
0	100	8.1	2.41	394*	5.47	77
pH-adjusted, leached						
85	15	6.6	5.85	88	7.34	41
70	30	6.2	8.37	68	8.76	33
30	70	6.9	7.07	88	7.97	46
0	100	7.0	4.74	103	6.81	48
LSD ($P \leqslant 0.01$)			1.46	93	2.52	30

† pH (1:5 solid : water extract) determined on subsamples of potted mixtures following harvest.
* Indicates plants showing B toxicity symptoms.

Table 4. Micronutrient composition ($\mu g\ g^{-1}$) of bean plant tops (Experiment 2)

Soil (%)	Ash (%)	Cu	Zn	Fe	Mn	Mo
100	0	20	69	283	37	9
Unleached						
85	15	17	39	268	45	13
70	30	15	27	250	28	15
30	70	20	31	237	24	21
0	100	22	40	196	15	21
Leached						
85	15	20	32	253	37	10
70	30	20	22	246	30	14
30	70	17	30	256	22	15
0	100	24	32	274	26	16
pH-adjusted and leached						
85	15	23	60	223	54	9
70	30	13	40	222	37	11
30	70	14	26	227	23	15
0	100	16	26	214	28	22
Normal range		5–20*	25–150*	50–250*	30–300**	–

* Jones[18].
** Geraldson *et al.*[13].

expressed mainly on the older leaves as a necrosis and scorching of the leaf margin especially near the leaftip.

The levels of hot water-soluble B in each ash are shown in Table 2 and, as might be expected, uptake of B by both species was greatest from ashes having higher levels of hot water-soluble B.

Experiment 2

Incorporating 30% or more of untreated Swanbank ash with the soil significantly reduced the yield of beans, whereas the yield of Rhodes grass was only significantly decreased at levels of $\geq$ 70% ash addition (Table 3). The yield reduction in beans was associated with increased tissue B concentrations and B toxicity symptoms (Table 3), whereas the levels of Cu, Zn, Fe, Mn and Mo in bean tops were normal and not affected by fly ash addition (Table 4).

Leaching the fly ash reduced the potential for boron toxicity, although bean plants in the 100% leached ash treatment produced significantly ($P \leq 0.01$) lower yields and toxicity levels in the plant tops compared to the loam alone (Table 3). The yield of Rhodes grass was not significantly affected by addition of leached ash to the soil. Adjusting the pH to 6.5 and subsequently leaching the fly ash completely removed the potential for B toxicity (Table 3).

Discussion

Untreated fly ash

The lower yields obtained in the untreated ash compared to the leached and pH-adjusted and leached ashes in both experiments are attributed mainly to B toxicity. Tissue levels of B in excess of 160 $\mu g\ g^{-1}$ have been reported as being toxic to beans[14]. In Experiment 1, unleached ashes from Munmorah, Tallawarra and Pt. Augusta resulted in bean plants with greater than 160 μg B g^{-1} tops (Table 2). Although a number of plants grown in the 5% unleached ash treatments had toxic levels of B, only in Pt. Augusta ash were yields significantly below those obtained in the corresponding pH-adjusted leached treatment (Fig. 1). On the other hand, with 10% ash addition to the sand, plants on the unleached treatments of all ashes except that from Callide exhibited B toxicity symptoms and had significantly ($P \leqslant 0.01$) lower yields than the pH-adjusted and leached treatments. An exception was the Callide fly ash in which tissue levels of B were low (Table 2), but yields of both beans and Rhodes grass were relatively poor (Figures 1 and 2). Plants grown on the Callide ash did not exhibit any identifiable symptoms except that they were a darker green than the other treatments. A possible explanation might be the lower available water capacity in mixtures of Callide fly ash and sand. Although watered to 10 kPa daily, more water stress would be expected in mixes with a lower available water range. Addition of fly ash (irrespective of source) to the sand increased the available water capacity (data not reported here); for example, the 10% ash addition increased the available water capacity of the sand by factors of 4.9 (0.9 to 4.4% by weight) and 9.2 (0.9 to 8.3% by weight) for Callide and Swanbank ashes respectively.

All bean plants grown in untreated ash:soil mixtures (Experiment 2) had B concentrations in excess of 160 $\mu g\ g^{-1}$ (Table 3). The appearance of classical B toxicity symptoms on the older leaves together with the very high content of boron in these plant parts (up to 1117 μg B g^{-1}) demonstrated that B toxicity was the major cause of the lower yields in these treatments. That the reduced yields for large additions of unleached ash were primarily attributable to B toxicity is further supported by the fact that levels of the micronutrients Cu, Zn, Fe, Mn and Mo in bean tops (Table 4) were normal and not affected by ash addition. There is little data in the literature regarding toxicity levels of B in Rhodes grass, but this species is known to be reasonably tolerant of salinity[26], and the lower concentrations of B in the tops together with the lack of pronounced B toxicity symptoms suggest that it may also be tolerant of high B. Although B toxicity symptoms

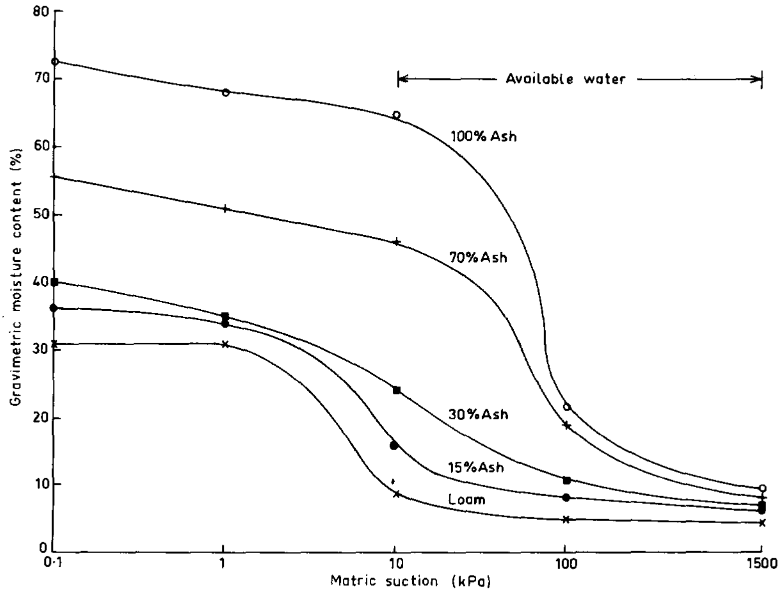

Fig. 3. Water characteristic curves for various mixtures of Swanbank fly ash and a sandy loam.

were observed at similar tissue concentrations of B in both species (Tables 2 and 3), Rhodes grass appeared to be able to tolerate higher B contents in the growing medium by taking up much less of the element than French bean. The extremely poor yield of Rhodes grass obtained in 100% untreated ash (Experiment 2) may possibly be due to a combination of factors such as high levels of B and poor aeration in this treatment. Soil water characteristic data for Australian fly ashes[3] has indicated that plant growth could be limited by lack of aeration in some fly ashes, and the low air capacity when Swanbank fly ash is wet to 10 kPa is evident from Figure 3.

The uptake of B by both species from unleached ashes in Experiment 1 was related to the level of hot water-soluble B in the ash (Table 2) indicating that this fraction might be used to diagnose the potential for B toxicity in Australian ashes. In establishing a guide to the suitability of British fly ashes for cropping purposes, it was considered that $< 4\,\mu g$ B g^{-1} 'available' boron would be non-toxic[17]; however, the use of such an index will depend on plant species and on the long term B release characteristics of the ash. For example, Swanbank fly ash contained $3\,\mu g\ g^{-1}$ hot water-soluble B, a level that might be considered non toxic, but it resulted in B toxicity and reduced yields (Experiment 2).

Although the untreated ashes were strongly alkaline (Table 1), most are poorly buffered[2], and it is considered unlikely that yields were markedly affected by pH. The addition of 10% untreated ash to the sand (Experiment 1) resulted in pH values at harvest of 8.9, 7.4, 7.0, 6.8 and 5.9 for Swanbank, Callide, Port Augusta, Munmorah and Tallawarra ashes respectively. In Experiment 2, the pH of the sandy loam was increased by the addition of Swanbank ash (Table 3) although, for any given ash treatment, the pH of the various ash:soil mixtures did not vary by more than 0.8 pH unit, and all values were within the range normally considered suitable for plant growth. Additionally, measurements of electrical conductivity in ash:sand and ash:soil mixtures indicated that salinity effects on plant growth would be negligible as all values were less than 0.60 mS cm^{-1} (1:5 solid: water extract).

Leached and pH-adjusted and leached fly ash

Although plant uptake of B was substantially reduced by leaching, the data suggest that the addition of large amounts of leached ash to soil would produce B toxicity in sensitive species and that the selection of species suitable for establishing vegetation on ash dams should take into account the plants' tolerance to high levels of B. Reduction in the B level of fly ash in dams by leaching may be possible; in a leaching study of one U.S. fly ash[21], it was shown that the B level could readily be reduced by leaching but the amounts of water required were so high as to render the process uneconomic.

In the pH-adjusted and leached fly ash treatments, tissue B concentrations were all well below that normally accepted as being toxic and, in Experiment 2, yields were equal or superior to that obtained for soil alone (Table 3). Laboratory studies have shown that the solubility of B greatly increased as the pH of fly ash suspensions decreased[9,21]. Although some leaching might be expected to occur during the weathering of fly ash in lagoons adjacent to power stations, laboratory experiments have shown that the pH of the ash does not decrease markedly during the leaching process[3].

In experiment 1, higher bean yields were obtained on 10% pH-adjusted and leached ash compared to the 5% pH adjusted-leached treatment for three ashes and, in the second experiment, the yields of bean tops in the 30% and 70% pH adjusted-leached ash treatments were significantly ($P \leqslant 0.01$) higher than the yield on the sandy loam (Table 3). There was a similar trend in the case of Rhodes grass, although the effects were not significant ($P \leqslant 0.05$). Since there is little likelihood that this effect is due to a chemical factor in these particular treatments, the positive response to ash addition is attributed to a physical effect. The most probable explanation is that the increased yields for these treatments are due to an increased available water capacity. As previously discussed, the available water capacity of the sand (Experiment 1) was increased by the addition of fly ash, and the moisture retention characteristics of each ash:soil mixture (Experiment 2) shown in Figure 3 demonstrate the marked increase in available water capacity at $\geqslant 30\%$ fly ash. Although 100% ash had the greatest available water capacity, yields on this treatment may not be the highest because of limited aeration, the change in water content from 10 kPa to near saturation (Figure 3) being only 9.7% of the total porosity.

The results of this study have demonstrated that B toxicity can limit plant growth on a representative range of Australian fly ashes although B uptake was dependent on plant species and rate of fly ash application. The data imply that, on soils deficient in B, plants will benefit from small applications of these ashes; deficiencies of B have been alleviated by the application of fly ashes to soils in USA[20,22]. Where B is adequate or in excess, however, caution should be exercised in utilizing unleached fly ashes, and the use of fly ash to improve soil characteristics should be undertaken with a knowledge of the B status. Although both experiments showed that the available water capacity of sand and soil can be markedly improved by additions of fly ash, the results indicate that mixing large proportions of untreated ash with soil will result in poor plant growth.

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