Section I

Bioavailability

1 Coal Fly Ash Application to Soils and its Effect on Boron Availability to Plants

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CONTENTS

1.1 INTRODUCTION

Fly ash, a by-product of coal combustion, is produced in large quantities in many countries and is partially disposed of in soils. Physically, fly ash consists mainly of silt-sized particles, is characterized by moderate to extremely high water-holding capacity, and possesses cementing properties. Chemically, fly ash is a ferro–alumino–silicate material and contains substantial amounts of macro- and micronutrients for plants (except C and N). Fly ash can be a strongly acidic or a strongly alkaline material, depending on its composition. Consequently, its application to soils can enhance soil fertility, improve soil's physical properties, and raise the pH of acid soils, if it is alkaline in reaction.

However, fly ash may cause undesirable environmental problems, i.e., unacceptable soil pH values, salinization, and B toxicity [1,2]. In fact, certain trace elements found in different fly ashes are considered to be potentially toxic in plants and animals [2], although, according to Page et al., [3] concentrations of trace elements in fly ash and soils are generally comparable, except those of B, Mo, and Se. Concentrations of these three elements in fly ash greatly exceed those generally found in soils.

Boron, an essential micronutrient for plant growth, is toxic at levels even slightly higher than the optimum for normal growth. Boron concentration in the soil solution plays an important role in plant nutrition because it is the determining factor of plant response [4]. Boron concentration in the soil solution, however, is buffered by B adsorbed onto soil particles [5]. Thus, knowledge of factors affecting B adsorption on and release from soil solids is important to understanding or predicting plant response when B-rich fly ash is applied to soils.

Application of fly ash to soil generally increases trace elements' concentrations to a degree that depends on fly ash properties, rate of application, and soil physicochemical characteristics. Among the potentially toxic trace elements in fly ash, however, only B has been associated with significant reductions in plant production under field conditions; fly ash B is water soluble and consequently may be readily absorbed by plants grown on soils amended with fly ash. In fact, many researchers consider B a major limiting factor for the beneficial utilization of fly ashes in croplands, especially unweathered fly ash [1]. In many cases, plant tolerance to fly ash is associated with B tolerance. Suggested measures to obviate detrimental effects to plants due to the agronomic use of fly ash include weathering of fly ash, followed by adequate drainage [1,2] or selection of species tolerant to B toxicity [2,6].

To evaluate the risk of B phytotoxicity in connection with the agronomic use of fly ash, knowledge relevant to B status in fly ash and soils, as well as to the factors controlling B availability, is needed. The objectives of this chapter are to compile and evaluate existing research and knowledge concerning: (1) concentrations and chemical behavior of B in fly ashes; (2) soil factors and constituents influencing the fate of B after fly ash application to soils; and (3) rates of fly ash application to soils that could result in B phytotoxicity or correction of B deficiency, in relation to properties of ashes and soils.

1.2 BORON IN FLY ASH

1.2.1 Boron Concentration in Fly Ash, as Affected by its Origin, Particle Size Distribution, and Degree of Weathering

Boron is among the trace elements with which fly ash is enriched [3], in comparison to other by-products of coal combustion. Goodarzi and Swaine [7] reported that, during the combustion of Netherlands coals (with an average B content of 35 mg kg^{-1}), B was highly concentrated in flue gases after desulfurization (average 1473 μg B m^{-3}) and relatively less concentrated in bottom ash (135 mg B kg^{-1}). Scrubbing by electrostatic precipitators reduced B content of flue gases to 237 μg m^{-3}, while the rest of B remained in fly ash. Furthermore, the same researchers reported that Australian bituminous coals have produced bottom ash with B concentrations of 40 to 80 mg kg^{-1} and fly ash containing 20 to 400 mg B kg^{-1}. Llorens et al. [8] studied the composition of Spanish fly and bottom ashes derived from a mixture of 95% subbituminous and 5% bituminous coal. They found that total B concentration in fly ash was almost 3.7 times higher than that in bottom ash and that water-extractable B of fly ash was 10.6 times greater than that of bottom ash.

Boron concentration in fly ash varies greatly. Table 1.1 summarizes the values of B content of fresh or weathered fly ashes derived from different types of coal, in various countries. It is reported that B concentration in fly ash is generally higher than that of other trace elements, ranging from 48 to 618 mg kg^{-1} [25]. Certain extremely high values of B content in fly ashes are reported in the literature. Cox et al. [29] and James et al. [27] found that B concentration in the ashes studied was at levels up to about 2000 mg kg^{-1}; Roy et al. [26] reported that B content in a western U.S. fly ash was 5000 mg kg^{-1}.

Among the trace elements contained in fly ash, B is the most soluble in water. Pagenkopf and Connolly [30] reported that more than 50% of the total B in fly ashes was water soluble. In a study involving 18 alkaline fly ashes in the U.S., James et al. [27] found that seven western fly ashes had

TABLE 1.1
Boron Concentrations in Fly Ashes

Country	Coal type	Fly ash (weathering / reaction)	B concentration (mg kg^{-1}) total	Water soluble	Ref.
Australia (Queensland, N. South Wales, S. Australia, W. Australia, Victoria)	Bituminous black or lignite brown	No / alkaline		1.1–41.6	9
		Yes / alkaline		0.1–4.2	
Australia (Queensland, N. South Wales, S. Australia)		No / alkaline		3.0–32.9	10
Australia	Bituminous		20–400		7
Australia		No / acid, alkaline		1.15–2.86 mg l^{-1}	11
Canada				42 mg l^{-1}	12
Greece	Lignite	Yes / alkaline		2.8–3.1	13
Greece	Lignite	No / alkaline	52		14
Greece	Lignite	No / alkaline	0.28–0.57		15
India		No	123		16
		Yes	150		
Slovenia	Brown coal	No	≅ 1		17
South Africa			23–600		18
Spain		No	61–339		19
UK			3–150 (mean 43)		20
UK				3–250	21
U.S. (9 States)	Bituminous or lignite	No	234–618		22, 23
U.S. (Kentucky, Ohio, Virginia, W.Virginia)			234–415		24
U.S. (Southeastern)		Acid		22	25
		Alkaline		50	
U.S. (Western)			10–618	24 (mean)	3
U.S. (Illinois)		No	870–1600		26
U.S. (Western)		Alkaline	800 (mean)		27
U.S. (Midwestern)		Alkaline	675 (mean)		27

TABLE 1.1
Boron Concentrations in Fly Ashes (continued)

			B concentration (mg kg^{-1}) total	
Country	**Coal type**	**Fly ash (weathering / reaction)**	**Water soluble**	**Ref.**
U.S. (Midwestern) (Illinois, Indiana, Kansas, Wisconsin, Michigan, Kentucky, Missouri, Iowa)		Alkaline	172–1480	27
U.S. (Alabama, Colorado, Dalaware, Georgia, Iowa, Kentucky, Maryland, Massachusetts, Michigan, Minnesota, Montana, N. Hampshire, N. Mexico, N. York, N. Carolina, Ohio, S. Carolina, S. Dakota, Utah, W. Virginia, Wisconsin)			10–900	28

an average total B concentration of 800 mg kg^{-1}, with 37% water leachable. The remaining 11 midwestern ashes had 675 mg kg^{-1} total B, 47% of which was water leachable.

According to Carlson and Adriano [2], concentrations of water-soluble B in fly ash may exceed the value of 250 mg kg^{-1} and 17 to 64% of the total B in fly ash is immediately soluble in water. Churey et al. [31] studied the solubility of As, B, Mo, and Se in aqueous equilibrates of many ashes. Boron was found to be more soluble than the other elements. On a weight basis, the most soluble trace elements of nine Illinois basin fly ashes were found to be B and Cd; the percentages of soluble matrix B ranged from 24 to 56% with an average of 44 ± 10% [26]. Based on a study of the mobility of water-soluble major and trace elements in four alkaline Spanish fly ashes, Querol et al. [32] reported that the leaching rate of B was the highest among 19 trace elements studied. Up to 78% of the B present in the fly ash samples was water soluble.

Boron concentration in fly ashes depends on a variety of factors, such as the nature of the element; the parent coal; the combustion conditions; the efficiency and type of emission control devices; and the degree of weathering [2]. The manner in which these factors affect B concentration in fly ash is discussed in the following paragraphs.

Certain elements during combustion are volatilized and then condense onto the surface of the ash particles as the flue gas cools. Boron has been classified among the trace elements that are partly or fully volatilized and partitioned between the fly ash and the combustion flue gas in the upper part of the combustion system [8]. Trace elements condense mainly on smaller particles because of greater surface area, as stated by El-Mogazi et al. [33]. Similarly, Elseewi et al. [34] and Pougnet et al. [18] reported that B concentration in fly ash is inversely proportional to the size of fly ash particles, meaning that B concentration increases as particle size decreases.

Boron concentration of two fly ashes was found to increase from 8 to 18 mg kg^{-1} and from 49 to 180 mg kg^{-1} as the fly ash particle size decreased from 51.7 to 7.7 μm and from 26.7 to 2.5 μm, respectively [35]. Hansen et al. [36] reported that total B in coal fly ash increased from 36.7 to 48.5 μmol g^{-1} as the particle size decreased from 20 to 2.2 μm. Boron was found to be more concentrated in the <53-μm fraction of fly ashes [3,37]. In addition, Halligan and Pagenkopf [38] reported that most of the available B of a fly ash was associated with the finest ash particles (<45 μm) and Hollis et al. [39] found that water-soluble B from a fly ash was concentrated in the smaller size fractions and only a small amount was dissolved from particles > 20 μm.

Boron concentration of fly ash depends also on B content of the coal burned. According to Pagenkopf and Connolly [30], the amount of B found in U.S. coal ashes varied from 5 to 200 mg kg^{-1}, depending upon the mine site. Ashes of eastern and midwestern (bituminous and subbituminous) coal deposits of the U.S. usually have lower B concentration than those from the western states (derived from subbituminous coals and lignite). Similarly, Adriano et al. [1] reported that total B content of fly ashes derived from bituminous and subbituminous coal and lignite were 36, 50, and 500 mg kg^{-1}, respectively.

The efficiency and type of emission control devices may affect the amount of the finest fly ash particles released into the atmosphere and, consequently, the amount of B released bound on these particles. Page et al. [3] reported that the estimates of the daily atmospheric emission of fly ash from two U.S. midwestern power plants, equipped with electrostatic precipitators, were 4 to 5 Mg day^{-1}; from another plant equipped with mechanical dust collector, it was 120 Mg day^{-1}. The latter station also had the greatest B emission. Gladney et al. [40], Llorens et al. [8], and Pagenkopf and Connolly [30] supported the idea that, except for B condensation on fly ash retained by the electrostatic precipitators, a significant amount of B probably is released to the atmosphere bound on uncaptured particles of fly ash. Specifically, Pagenkopf and Connolly [30] reported that as much as 71% of the total B present in coal may be lost to the atmosphere upon combustion.

Conversely, Goodarzi and Swaine [7] suggested that, because B is partly volatile, small amounts of B are expected to be emitted into the atmosphere through fine fly ash particles. These researchers studied the deposition of B around a power station located near Sydney, Australia, for 3 years. Their results showed that B deposition on land, over the whole period, ranged from <0.01 to 13 mg B m^{-2} and that most B was deposited near the power station, within a radius of about 5 km, with a tendency to decrease with distance from the station.

Weathering of fly ash reduces soluble B [2], thus minimizing the risk of B phytotoxicity to plants grown on ash deposits or in soils amended with fly ash. However, the beneficial impact of fly ash weathering on plant growth, with respect to B, depends upon the initial B content of fly ash and the rate of B leaching. Weathering of fly ash under laboratory or natural conditions and its effect on plant growth are discussed in more detail in the next sections.

1.2.2 Fly Ash Constituents Associated with B and Mechanisms of B Release and Retention

Fly ash consists mainly of alumino–silicate materials, 70 to 90% of which are glassy spheres; the remainder consists of quartz, mullite, hematite, magnetite, calcite, gypsum, and anhydrite [1,41]. Furthermore, tourmaline, a mineral containing B, was identified and the presence of B salts such as borax, rhodium boride, boron arsenite, and boron phosphate was suggested [1].

Section 1.2.1 mentioned that a significant proportion of total B in fly ash seems to be readily water soluble. It was found that at least two independent B chemical species must be present in fly ash, i.e., soluble and insoluble; the first one must not be present in bottom ash [29,34]. Narukawa et al. [35] conducted fractionation experiments and concluded that most of the B chemical species in fly ash were water soluble. In order to explain the high mobility of fly ash B, James et al. [27] suggested that the predominant forms of B in fly ash are probably very soluble borates and less soluble borosilicates, but Pagenkopf and Conolly [30] claimed that the B-soluble species in fly ash are borates and boric acid. In addition, Gangloff et al. [42] attributed the rapid leaching of B observed from fly ash–soil mixtures to the presence of a moderately soluble borate salt residing on fly ash surface.

Several researchers conducted experiments to determine the components of fly ash connected to highly or less soluble B species. Elseewi et al. [34] reported that the low solubility B fractions may be associated with Fe, Al, and Mg oxides, which exhibit high affinity for B existing in fly ash at relatively high concentrations. Narukawa et al. [35] reported that the majority of B chemical species (including the water-soluble ones) were associated with Fe and Mn oxides in acidic fly ashes and with carbonates in alkaline fly ashes. Warren et al. [43] studied the release of B from an alkaline fly ash in relation to the pH of ash aqueous suspensions containing $HClO_4$. They observed that B dissolution increased with decreasing pH of the suspension and concluded that B released from the fly ash at $pH < 6.0$ seemed to be associated with Ca and Mg species in the ash, which have high affinity to B and not with alumino–silicate or silicate glass material. In addition, Plank et al. [44] suggested that the less soluble B species probably are connected to the vitreous phase of fly ash.

The association of soluble B with Ca or Fe species and of less soluble B with Al–Si material in fly ash could be supported by the scheme of secondary minerals formation during acid weathering of fly ash proposed by Warren and Dudas [41]. They reported that CaO is transformed to less soluble minerals, such as calcite and possibly aragonite and gypsum, and Fe compounds are dissolved; followed by precipitation as an amorphous oxyhydroxide; Al–Si material is solubilized; and followed by precipitation of an amorphous clay material identified as protoimogolite.

To explain the high solubility of fly ash B under acidic conditions, Dreesen et al. [45] suggested that B is among the trace elements that are predominant at the surface of fly ash particles. Moreover, Elseewi et al. [34] reported that the water-soluble B fraction, which is considered plant available, is probably associated with the outer surfaces of fly ash spheres; the less soluble fraction is associated with the inner matrix of fly ash and in compounds of low solubility. Based on data obtained from fly ash leaching experiments, Querol et al. [32] concluded that the leaching trends of trace elements, including B, were consistent with the dissolution of small particles or coatings on the surface of the ash solid phases rather than with the dissolution of a homogeneous glass phase.

Dudas and Warren [46] proposed a submicroscopic model for solid and thick-walled glassy particles of fly ash, which comprise the bulk of any coal fly ash. The model is consistent with the results of fly ash weathering and leaching experiments. It explains the behavior of fly ash elements on the basis of their partitioning into a reactive exterior glass surface and subsurface and into an interior, less reactive glass matrix, which weathers at a slow rate. Elements readily leached from ash, like B, are mainly associated with the exterior reactive surface of ash particles. The partitioning of elements is related to the forms of each element in the coal and to combustion conditions.

These researchers stated that B occurs in solid form as hydrous borates in shale fragments mixed with coal. During combustion, the hydrous borates would be transformed to particles of simple oxides such as B_2O_3, which then could fuse with the reactive exterior of ash particles. Moreover, it was proposed that most of the elements contained in the carbonaceous material can exhibit similar behavior; according to Boyd [47], a significant fraction of B that occurred in coal was organically bound.

Although the majority of studies are focused on B release from fly ash, B retention by fly ash constituents has been also investigated. Zhang and Reardon [48] attributed the reduction of B concentration in fly ash leachates to ettringite formation during leaching. Also, B concentration in the leachates of a lime-treated fly ash decreased markedly, and this decrease was attributed to hydrocalumite identified in the leached fly ash.

Pagenkopf and Connolly [30] proposed three possible physicochemical reactions that may influence B release from coal fly ash:

- B adsorption by hydrous oxides
- Solubilization of metal borates
- Formation of surface coatings that occlude B within the ash particles

According to these researchers, adsorption of B by the alumino–silicate matrix seems to be the major mechanism for B retention by ash particles. In addition, Hollis et al. [39] reported that coprecipitation of B with $CaCO_3$ is also a possible mechanism of B retention in alkaline fly ashes.

1.2.3 Factors Affecting B Release from and Retention by Fly Ash

Total B content of fly ash; ash particle size (see Section 1.2.1); contact time and ratio of ash to leachates; and pH are the main factors influencing B release from and retention by fly ash particles. They are discussed in more detail in the next paragraphs.

Water-soluble concentration of B was highly correlated with its total concentration in soft coal fly ash [31]. Furr et al. [28] reported that B absorption by cabbage (*Brassica oleracea*) grown on soil amended with U.S. fly ashes at a rate of 7% w/w was strongly correlated with the ash total B content. On the other hand, Pougnet et al. [18] reported that leached B from 31 strongly alkaline coal fly ashes equilibrated with water at a ratio 1:100 for 20 h ranged from 11 to 39% of the total B in fly ashes. No relationship was observed between the total B content of the fly ashes and the percentages of B leached.

The rate of B release from fly ash seems to decrease with time. Jones and Lewis [49] and Halligan and Pagenkopf [38] observed that the amount of B released from coal fly ashes exhibited a rapid initial increase; the rate of release decreased with time and eventually reached a plateau. Townsend and Hodgson [20] studied the change of B concentration in fly ash–water extracts over a period of 9 h. Their data showed that B in water extracts was sharply increased during the first 2 to 4 h and then decreased. Hollis et al. [39] found that the water-soluble B concentration in extracts derived from an alkaline fly ash decreased from 3.7 to 0.7 mmol dm^{-3} with increasing contact time from 0.5 to 96 h.

It was observed that the rate of B release increased as the dilution of ash–water suspensions increased [34,38]. This increase was attributed to the enhanced migration of B from the inner to the outer surfaces of fly ash particles, due to dilution.

Many researchers have studied the solubilization of B from fly ash under different pH values [3,10,29,34,35,37,39,45,50–53]. The extractability of B from fly ash was found to be strongly and inversely related to pH (described in detail in the next paragraphs).

Boron in a strongly alkaline fly ash was extracted with water and different acid and alkaline solutions. The higher percentages of extractable B were found in strongly acidic pH media. Specifically, 94% of fly ash B was extracted with 0.1 *M* citric acid (pH = 3.6), whereas only 1.5% was extracted with water (pH = 11.9) [45]. In an experiment investigating the release of several trace elements from a British fly ash by using several extraction techniques, it was found that B concentration in the extractant solution decreased as pH increased from 4.6 to 9.3 [50]. In addition, Cox et al. [29] reported that the leaching rate of fly ash B was higher into acid solutions; total soluble B did not depend on the pH over the range of 6 to 8, but it was decreased at strong alkaline pH.

Also, Page et al. [3] found that, although B concentration in strongly alkaline fly ash–water extracts (pH > 12) was very low (<0.6 mg l^{-1}), it increased significantly (65 mg l^{-1}) when the pH decreased to 6.5. Similar results were reported by Elseewi et al. [51] and Phung et al. [37]. In a relevant work, Elseewi et al. [34] used water and 0.01 *N* NaCl, both neutral and acidified, as B extracting solutions from fly ash. They found that the amounts of B extracted by the acidified NaCl solutions were substantially higher than those extracted by water or the neutral electrolyte. The maximum percentage of fly ash total B, extracted with water, was 27.4%; that extracted by the acidified NaCl was 41.4%.

In addition, Hollis et al. [39] found that, at pH 9, three extractions with water removed only 60% of the fly ash total B; however, at pH 6, two extractions removed all total B contained in the ash, with the highest amount of B removed in the first extraction. Narukawa et al. [35] found that the highest percentages of B leached from acidic and alkaline fly ashes did not depend on the initial pH of the ash and were obtained by using an acid solution (pH = 4), in comparison to water (pH similar to that of the ash) and to an alkaline solution (pH = 12).

Weathering, in conjunction with the final pH, seems to affect B availability in a different way in acidic and alkaline fly ashes. Thus, Khandkar et al. [52] reported that hot water-extractable B of three acidic fly ashes derived from Gondwana coals decreased after weathering; that of an alkaline fly ash derived from lignite coal increased. This was attributed to the fact that, during weathering, the pH of the acidic fly ashes changed to alkaline, but that of the alkaline fly ash decreased to the acid range. In a relevant study with two alkaline fly ashes, Kukier et al. [53] found that the amounts of hot water-extractable B increased with increasing acidity of the boiling solutions. In another similar study with five Australian strongly alkaline unweathered fly ashes, Aitken and Bell [10] reported that hot water-extractable B ranged from 3.0 to 32.9 mg kg^{-1} in the fresh ashes, but decreased to 0.3 to 12.2 mg kg^{-1} when the ashes were leached with deionized water, and to 0.3 to 4.7 mg kg^{-1} when ashes were adjusted to pH 6.5 and subsequently leached.

All the previously mentioned findings agree that the solubility of fly ash B is strongly and inversely related to the pH of the extracting solution. As the pH decreases, the dissolution of fly ash particles is enhanced, and the smaller particles are dissolved more quickly than the bigger, starting from the surface to the interior of the particle. Consequently, these findings are in agreement with those mentioned in Section 1.2.2 that a high amount of the B in fly ash is in available forms; is associated mainly with the smaller particles; and is located at the surface rather than in the interior of fly ash particles. Most of the relevant studies referred to pH values ≥ 4.0. Because the solubility of Al–Si matrix of fly ash is rather low at these pH values, it should be concluded that the readily available B from fly ash is probably associated with other than the alumino–silicate phase. This conclusion is also in agreement with the findings reported in the Section 1.2.2.

1.2.4 PLANT GROWTH ON FLY ASH WITH RESPECT TO ITS B CONTENT

The main factors limiting plant growth on fly ash deposits are excessive B; high pH; high salinity; and lack of N and, to some extent, P. In addition, indurated layers of ash produced by compaction and pozzolanic action may inhibit the normal growth of the root system. Agricultural and horticultural crops have been classified on the basis of tolerance to fly ash. According to Hodgson and Buckley [54], Chenopodiaceae are all highly tolerant to fly ash, and Leguminosae, Cruciferae, and Graminae species show considerable variation in their capacity to tolerate fly ash. It is reported that grouping species in relation to their ash tolerance is similar to grouping them on the basis of B requirements. Although the ability of plants to grow on fly ash indicates mainly their tolerance to B excess, the role of soluble salts, unstable crumb structure and macro- and micronutrient deficiencies should also be considered.

On the basis of data from British fly ashes, Hodgson and Townsend [55] proposed certain B concentration ranges for plant growth on fly ashes. Specifically, they proposed that concentration of hot water-extractable B at levels less than 4 mg kg^{-1} be considered as nontoxic; 4 to 10 mg kg^{-1} as slightly toxic; 11 to 20 mg kg^{-1} as moderately toxic; 21 to 30 mg kg^{-1} as toxic; and greater than 30 mg kg^{-1} as highly toxic. Also, Townsend and Gillham [21] suggested that hot water-extractable B levels in fly ashes higher than 20 mg kg^{-1} are probably toxic to most agricultural crops; more sensitive crops such as barley (*Hordeum vulgare*), peas (*Pisum sativum*), and beans (*Phaseolous vulgaris*) could show symptoms at values as low as 7 mg kg^{-1}. However, such data do not take into account the long-term B release characteristics of ash, especially unweathered fly ashes, and the genetic characteristics of plant species, concerning their behavior to B excess. For example, an Australian fly ash containing 3 mg kg^{-1} hot water-extractable B — a level considered nontoxic — resulted in B toxicity and reduced yields of French beans and Rhodes grass (*Chloris gavana*) [10].

As Section 1.2.1 mentioned, weathering of fly ash reduces B content. However, the time needed for reducing B concentration in fly ash at acceptable levels for plant growth, under natural conditions, varies widely. Some reports in the literature suggest a period from a few to several years of fly ash aging, depending on the initial B content of fly ash and the climate. Jones and Lewis [49], for example, reported that in a fly ash stock pile, B content of some recently deposited fly ash was 216 mg kg^{-1} and that of 25-year-old ashes was 4.3 mg kg^{-1}. Boron content of wild white clover (*Trifolium repens*) grown on ash decreased with increasing ash aging and became similar to that of the soil control in the 25-year-old ash.

According to Townsend and Gillham [21], weathering of fly ash with moderately high initial B content for 4 years could reduce B to acceptable levels. Burns and Collier [56] developed a simulation model to predict the period required to leach B from the top 30 cm of a coal ash deposit in the U.K. This model predicted that B concentration would decrease at acceptable levels for most crops after 5 to 15 years. According to Nass et al. [57], B concentration in grasses grown on 20- and 30-year-old fly ash deposits was lower than that obtained for plants grown on fresh fly ashes, but higher than the values considered normal for these specific species.

In general, plant species grown on fly ash deposits weathered for certain years attained better growth and absorbed B at levels probably high but nontoxic. The growth of species in relatively weathered or fresh fly ash was limited by B toxicity, among other factors. However, the opposite cannot be precluded, depending on the fly ash B content and the plant species.

Several cases of different species grown well on weathered fly ash deposits are reported in the literature. It was found that B concentration of white sweet clover grown on a coal fly ash containing 7.5 mg B kg^{-1} was slightly higher (51 mg kg^{-1}) than that grown on a soil containing 5.2 mg B kg^{-1} (45 mg kg^{-1}) [58]. In a study with grasses and legumes growing on four soil-capped ash landfills in New York, Weinstein et al. [59] found elevated levels of B in most of the plants, with generally higher levels in the legumes than in grasses. To explain this difference, they hypothesized that the deeper rooted legumes had probably penetrated the underlying ash deposit.

On the other hand, Woodbury et al. [60] found that B concentrations of several plant species, i.e., bird's foot trefoil (*Lotus corniculatus*); red clover (*Trifolium pratense*), timothy (*Phleum pratense*), orchard grass (*Dactylis glomerata*), velvet grass (*Halcus lanatus*); and several fescues (*Festuca* spp.) grown on a soil-capped ash landfill ranged at levels similar to the soil control (29 to 53 mg kg^{-1} in the legumes and 2 to 11 mg kg^{-1} in the grasses). Conversely, growth of cucumber (*Cucumis sativus*), which is considered a semitolerant crop to B toxicity, was suppressed in a weathered acidic fly ash, although the ash had a low B content (total B 28 mg kg^{-1} and water-extractable B 3.7 mg kg^{-1}). After 8 weeks, all plants exhibited certain toxicity symptoms and plant biomass was significantly less compared to the control soil. It was concluded that B toxicity was the primary cause for plant growth suppression because B concentrations in ash grown plants were tenfold of the control and exceeded the B toxicity threshold for cucumber (>300 mg kg^{-1}) [61].

In addition, several woody species have been tested in fly ash deposits. In certain cases, the deeper rooted system was proved to be the main factor preventing B accumulation at levels higher than those considered toxic, although the ash was enriched in B. For example, *Polpulus robusta* and *Picea sitchensis* grown on two ash deposits containing 14 and 100 mg B kg^{-1}, respectively, did not exhibit severe B toxicity symptoms. This was attributed to the fact that B concentration at depths below 30 to 40 cm was low [54]. Similarly, eight woody species — European black alder (*Alnus glutinosa*); sweet birch (*Betula lenta*); sycamore (*Platanus occidentalis*); sawtooth oak (*Quercus acutissima*); cherry olive (*Elaeagnus multiflora)*; autumn olive (*Elaeagnus umbellata*); silky dogwood (*Cornus amomum*); and gray dogwood (*Cornus racemosa*) — grown on a strongly acidic fly ash did not show B toxicity symptoms, although plant B levels were elevated [62].

Carlson and Adriano [63] reported similar results for sweet gum (*Liquidambar styraciflua*) and sycamore growing on a 20-year-old fly ash wet basin (pH = 5.6). Trees growing on the ash attained better growth, even though they had higher trace element concentrations in comparison to the control soil. As far as B is concerned, elevated concentrations were observed in trees growing on the ash (three times the control); however, in almost all cases, B levels in the foliage were below 100 mg kg^{-1}. The differences between fly ash-wet basin and soil observed in foliar B concentrations were attributed to differences in B substrate concentrations.

The deleterious effects of fly ash, especially the unweathered, on plant growth due to high B content can be avoided by weathering or by mixing the fly ash with an inert medium. Holliday et al. [64] conducted a pot experiment with oat (*Avena vulgare*) grown on an inert medium mixed with a strongly alkaline fresh fly ash (pH = 9.0) and on the same ash treated with acid (pH = 6.4), at rates up to 100%. They found that B toxicity symptoms were obvious in the plants grown in the inert medium with fresh ash ≥ 6% and acid-treated ash ≥ 25%. At these rates, B concentrations in the biomass were 260 and 310 mg kg^{-1} for the untreated and the treated fly ash, respectively.

Similar research was carried out by Townsend and Gillham [21] by means of a small-scale field experiment with cereals, grasses, legumes, and other crops, using initially fresh and weathered fly ash, amended or not with silt. Among the species studied, red clover; white clover and Lucerne; timothy; cocksfoot and ryegrass (*Lolium perenne*); and potatoes (*Solanum tuberosum*) have been grown well for a number of years, apart from failures in the early years on the new ash plots (with no silt), attributable to excess B. The improvement of all crops' performance with years was attributed to a decrease of B content of the ash by weathering.

Aitken and Bell [10] studied the uptake of B by French beans and Rhodes grass grown on alkaline fly ash–sand mixtures in a pot experiment. The five fly ashes used were untreated, leached, or adjusted to pH 6.5 and subsequently leached and mixed with sand at rates of 5 and 10% w/w. The untreated ashes resulted in lower yields than the leached and pH adjusted and subsequently leached for both species; this was attributed mainly to B toxicity because plant B uptake and hot water-extractable B were higher in the untreated ashes. For both levels of ash addition and both species, B concentrations and uptake decreased in the order: untreated ash > leached ash > pH-adjusted and leached ash.

Although B phytotoxicity is a possible risk for plants grown on unweathered fly ashes, especially those having high B content, the opposite is also true as stated by Nass et al. [57]. For 6 years, they studied the growth of a mixture of grasses (*Lolium perenne, Festuca rubra commutata,* and *Phleum pratense*) and white clover, in lysimeters filled with three fresh fly ashes that differed in their reaction (alkaline, neutral, and acidic). Boron concentrations in plant tissues were always below 33 mg kg^{-1} and only concentrations higher than 50 mg kg^{-1} would cause B toxicity.

Some cases of detrimental effects on seedling growth in fly ash, due to trace elements, are also reported in the literature. Excessive levels of certain trace elements, including B, impaired the growth of lettuce (*Lactuca sativa*) seedlings on a British neutral fly ash [50]. In addition, Shulka and Mishra [65] attributed the deleterious effects on the seedlings of corn (*Zea mays*) and soybean grown in nutrient solution amended with 2.5% Indian alkaline fly ash to B or heavy metals.

1.3 BORON AVAILABILITY TO PLANTS AS INFLUENCED BY FLY ASH APPLICATION TO SOILS

1.3.1 Soil B

Boron is a micronutrient, essential for plant growth, for which the range of deficiency, sufficiency, and toxicity is too narrow. According to Evans and Sparks [66], B concentrations in soil solution of <1 mg l^{-1} are considered deficient; 1 to 5 mg l^{-1} sufficient; and >5 mg l^{-1} toxic for the normal growth of most plants. Keren and Bingham [6] suggested that soil concentrations of hot water-extractable B (B availability index) exceeding the value of 5 mg kg^{-1} are considered phytotoxic to most crops. Boron concentration in the soil solution is very important for plant nutrition because plants respond only to B concentration in it [4]. However, B of the soil solution is in equilibrium to B adsorbed by soil particles. Plants obtain B from the soil solution and the adsorbed pool of B acts as a buffer against changes in solution B [5]. Thus, it is important to know the soil constituents absorbing B and the soil factors affecting B adsorption in order to predict or prevent drastic changes in soil B content caused by external sources (e.g., by soil application of fly ash).

Boron in the soil solution at the common range of soil pH exists as two chemical species, i.e., boric acid, H_3BO_3, and borate anion, $B(OH)_4^-$; the latter appears at the alkaline range of soil pH and has greater affinity to soil colloids. Both species are quite water soluble [6,67]. The soil constituents that adsorb B are Al and Fe oxyhydroxides, clay minerals, $CaCO_3$, and organic matter. Specifically, clay minerals' B adsorption capacity has been found to increase in the order: kaolinite < montmorillonite < illite. Various mechanisms have been proposed to explain B adsorption by Al and Fe oxyhydroxides, edges of clay minerals, and organic matter, among which ligand exchange seems to be the dominant. In addition, B coprecipitation with $CaCO_3$ has been reported as a B sorption mechanism. Several soil factors influence B retention by and release from soil constituents, including [5,67]:

- pH
- Texture
- B concentration and ionic composition of the soil solution
- Cation exchange capacity
- Exchangeable ions
- Other anions
- Soil moisture
- Wetting and drying
- Temperature

1.3.2 Soil Factors Affecting Availability of Fly Ash B to Plants

The same soil factors affecting the availability of soil B affect also the availability of B released from fly ash added to the soil. Of all factors mentioned in Section 1.3.1, soil pH is probably the most important factor, followed by soil texture. Boron adsorption by soil solids increases as the soil pH increases, reaching a maximum at the pH range of 8.5 to 10. Soils with low clay content adsorb less B, and B in sandy soils is leached more easily and rapidly than in clayey soils [5,67].

Fly ash application to soils results in an increase (alkaline ash) or a decrease (acidic ash) in pH. Through that, in conjunction to soil texture, it affects B adsorption or B leaching. Final acid or neutral values of soil pH and coarse texture promote rapid leaching of B from the soils, and alkaline values and fine texture promote B adsorption by soil colloids. Both processes may be utilized in removing excessive amounts of B from the soil solution to avoid risk of B phytotoxicity. In both cases, however, the final result depends significantly on fly ash B content and the rate of fly ash addition.

Several studies have showed that incorporating fly ash into a coarse textured soil and allowing for subsequent leaching would result in the removal of certain potentially phytotoxic elements from the root zone, thus minimizing threats to crops [37,42,68–70]. In most of these studies, the pH of the leachates or the ash–soil mixtures was lower than that connected to B adsorption maximum. In a leaching experiment in columns, with an acid sand and a calcareous sandy loam soil amended with 5% w/w strongly alkaline fly ash of high B content, it was found that B was leached from the fly ash-amended acid sand more readily compared to the calcareous soil. The pH of the leachates was similar to the initial pH of the soils during the whole leaching period. However, at the end of the experiment, less than 20% of the total B was removed from both soils [70].

In another experiment with an alkaline fly ash added to three soils — one acid sand and two calcareous soils (a loamy sand and a silt loam) — at rates up to 1%, water-soluble B increased in all cases. The calcareous soil with the highest pH (8.2) and the finest texture (silt loam) was the least affected by fly ash application [37]. In leaching experiments with a loamy sand soil, Ghodrati et al. [68] amended soil with two alkaline fly ashes at a rate of 30% w/w and observed that the initial B concentration in the leachates was high, but decreased to background levels after about 30 cm of water had passed through the soil. More than 92% of the B initially present in the ash-amended soil had leached from ash–soil mixtures after leaching with 150 cm of water. Similar experiments and results have been reported [69].

In another experiment, Gangloff et al. [42] added unweathered alkaline (pH = 8.4) fly ash, with low total B, in an acid (pH ≅ 5.0) loamy sand soil at a high rate (≅ 662 Mg ha^{-1}). Their goal was to study the leachability of B under field conditions, with lysimeters installed at a depth of 120 cm. A peak B concentration of 4.8 mg l^{-1} in the leachates occurred after 35 to 40 cm of cumulative rainfall. At this point, the pH of the leachates was extremely acidic (pH < 4.0), although it was alkaline (pH ≅ 8.0) in the beginning. Approximately 82 cm of cumulative rainfall was needed to reduce B concentration in the leachates from ash-amended plots to initial levels (≅1 mg l^{-1}).

At the same field, the same researchers [42] established microplots in order to characterize leachate properties of fly ash-amended soil under more controlled conditions. The same fly ash was applied at a higher rate (950 Mg ha^{-1}) and lysimeters were established at various depths to 120 cm. A peak B concentration of approximately 8.5 mg l^{-1} was observed in the leachates at 15 cm depth after 18 cm of irrigation water. Leachate samples from the lysimeters installed at depths of 15, 30, and 60 cm generally had B concentrations much higher than those collected at 120 cm. The pH of the amended microplots was less than 8.0 during the course of this study.

Although leaching of fly ash-amended soils coarse or moderately coarse in texture is expected to reduce soluble B and consequently plant available B, this is not always the case. A large proportion of B added in the form of fly ash might be leached but the remaining could be high enough to support elevated B concentrations in the plants grown in ash-amended soils. This might be due to high B content and high fly ash application rates. In a greenhouse study, a loamy sand, moderately acidic soil was amended with alkaline fly ash at rates up to 40% w/w (equivalent to 600 Mg ha^{-1}) and subjected to four leaching regimes (equivalent to 0, 25, 50, and 100 cm of rainfall). Of particular importance was the rapid leaching of B from ash–soil mixtures. After leaching, corn was grown in fly ash–soil mixtures. Leaching enhanced corn growth, but did not result in equivalent dry matter yield to that obtained from the control soil. This was attributed to the fact that B concentrations in corn grown in the leached ash-amended soils decreased compared to the unleached, but remained at levels that could be considered high [69].

Application of alkaline fly ash with a high B content to soils is expected to raise soil pH and, consequently, enhance B adsorption by soil constituents, thus resulting in low levels of B in the soil solution. This hypothesis was tested by Matsi and Keramidas [71], who studied the changes in B adsorption characteristics of three soils (two acid and one calcareous) upon addition of two Greek, alkaline fly ashes, by using adsorption and desorption experiments. The fly ashes were added to the soils at rates up to 5% w/w (equivalent to $\cong$100 Mg ha^{-1}). Because both fly ashes did not contain appreciable amounts of B (hot water-extractable B was 2.78 and 3.12 mg kg^{-1}), B was externally added to the fly ash–soil mixtures used in the desorption experiment. Fly ash application increased only B sorption capacity of all soils, but not the strength of B retention by soil solids. Within a desorption period of 120 h, 80 to 100% of the adsorbed B was released.

These findings suggested that, upon fly ash addition to soils, any increase in B sorption capacity is not necessarily accompanied by an increase in the strength of B retention by soil constituents; consequently, added B might remain in a loosely held condition onto soil solids and could be easily released into the soil solution. Martens et al. [22] reported that application of three alkaline fly ashes containing high levels of total B at various rates increased B uptake by alfalfa (*Medicago sativa*) grown on a silt loam soil, despite the increase in soil pH. They concluded that B in fly ash is sufficiently mobile to overcome any decrease in B availability resulting from the increase in soil pH. In a similar study with an alkaline fly ash with high content of total B and an acidic clay soil, Warren et al. [43] found that B adsorption increased because of increase in pH (from 4.5 to 5.9); however, even at the highest application rate (167 Mg $ha^{-1} \cong$ 8.35% w/w), adsorbed B accounted for only 10% of the total B.

Most of the findings in B adsorption studies in fly ash-amended soils suggest that, upon ash application to soils, B adsorption by soil particles plays a rather insignificant role in removing B excess from the soil solution. This occurred at all pH ranges common in soils, even at the alkaline pH range where B adsorption maximum occurs. Consequently, instead of relying on adsorption, leaching with adequate drainage is a more effective strategy in order to prevent B phytotoxicity due to fly ash addition in soils, especially in the cases of ashes with high B content.

1.3.3 PLANT GROWTH IN FLY ASH-AMENDED SOILS WITH RESPECT TO B

Using alkaline fly ash as a liming material to acid soils is probably the most common agronomic utilization of fly ash. In addition, cases of alkaline or acid fly ash application to soils differing in their physicochemical characteristics to improve soil fertility or soil physical properties are also frequently reported in the literature. In all cases, however, caution is needed with respect to B phytotoxicity risk. Although several studies reported in the previous sections of this chapter proved the high plant availability of fly ash B, this is further demonstrated by the enrichment ratio (ER). The ER of an element is calculated by dividing the elemental concentration of the plant grown in a treated soil with that grown in the untreated. The higher the ER for an element is, the greater is the plant adsorption of the particular element due to treatment.

Adriano et al. [1] determined ER for 27 elements for plants grown in soils and fly ash-amended soils. They reported that the ER values for most of the elements were $\cong$ 1.0 (meaning no effect on elemental absorption). However, several potentially hazardous elements, such as As, Ba, B, Mo, Se, Sr, and V, showed remarkable concentrating effects when plants were grown in fly ash-treated substrates (ER $\cong$ 3 to 8 and, specifically, for B $\cong$ 5.0). Tolle and Arthur [72] reported that plant uptake of trace elements due to fly ash addition reached plant toxic levels for only one element: B. Among ER values determined for 25 elements, exceptionally high values (ER > 15) were noted only for four elements, one of which was B.

1.3.3.1 Cases of B Phytotoxicity

It is postulated that B phytotoxicity may persist for a number of years after fly ash application to soils [44]. Cases of B toxicity caused by fly ash application to soils are summarized in Table1.2. Boron toxicity was evident mainly by yield reduction or poor plant growth in conjunction with elevated B concentrations in plant and soils. However, B toxicity symptoms were obvious in plants only in certain cases. Although different rates of fly ash application are reported, as can be seen in Table 1.2, the usual rates have not exceeded the value of 10% w/w (equivalent to ≅ 200 Mg ha^{-1}; Table 1.2); in most of the cases, fly ash was unweathered [10,34,53,72,73,79–81].

It will be evident from the following discussion that the risk of B phytotoxicity is mainly connected to the agronomic use of unweathered rather than weathered fly ash because adequate weathering is expected to reduce B content of ash significantly (see also Section 1.2.3 and Section 1.2.4). Phung et al. [82] tested the possibility of using a fresh, strongly alkaline fly ash as a liming material to a strongly acidic, silty clay soil. Ash application at the highest rates (5 and 10% w/w) increased soil B at levels that could be considered toxic to sensitive plants. Martens and Beahm [81] compared the effects of a weathered and a fresh ash applied to a strongly acidic silt loam soil. They found that addition of the weathered ash at rates up to 144 Mg ha^{-1} had no harmful effect, but fresh ash at rates of 96 to 144 Mg ha^{-1} resulted in B toxicity to corn plants.

In addition, in a glasshouse experiment with French beans and Rhodes grass, Aitken and Bell [10] used an Australian fly ash (untreated, leached, or adjusted to pH 6.5 and subsequently leached) as an amendment (0 to 70% w/w) for a sandy loam soil. They found that, for both species, heavy applications of untreated fly ash (≥30% for beans and 70% for Rhodes grass) resulted in poor plant growth, primarily due to B toxicity. The risk of B phytotoxicity was reduced by leaching the fly ash and even more by pH adjustment and subsequent leaching, prior to soil addition. Boron concentrations in plant tissues of both species were above 100 mg kg^{-1} for almost all untreated ash treatments and below 100 mg kg^{-1} for almost all pH adjusted and leached ash treatments.

1.3.3.2 Cases of B Deficiency Correction

Although B phytotoxicity due to soil application of fly ash is the common case reported in the literature, beneficial effects of the agronomic use of fly ash, such as alleviation of B deficiencies for several plants, have also been reported and are summarized in Table 1.3. The usual rates of ash application to soils were similar to those reported in the previous section (up to 10% w/w ≅ 200 Mg ha^{-1}). According to Bradford [91], if a B concentration in plants equal to about 200 mg kg^{-1} is considered the threshold of toxicity for most crops, then B levels in plants shown in Table 1.3 were much lower and, in most cases, were lower than 100 mg kg^{-1} [13,22,25,44,83,86–88,90].

The availability of B from fly ash has been compared to common B fertilizers (i.e., borax) by means of pot and field experiments [22,23,25,87]. In a pot experiment, Martens et al. [22] found that application of three alkaline fly ashes containing high levels of total B (319, 415, and 618 mg kg^{-1}) at various rates increased B uptake by alfalfa grown in a silt loam soil, at levels similar to those resulted from the application of borax at equal rates. Similarly, Plank and Martens [25] used two U.S. fly ashes (acid and alkaline) with high B content as B sources for alfalfa in a 3-year field experiment and compared the results to those obtained by the use of borax. Fly ashes were applied at rates equivalent to 1.7 and 3.4 kg B ha^{-1} (based on their total B content) in a single dose in the beginning of the experiment; borax was applied in the beginning of each growing season. They found that yield and B uptake by alfalfa was significantly increased upon application of both fly

TABLE 1.2
Cases of Detrimental Effects of Fly Ash on Plant Growth with Respect to B

Plant species	Soil characteristics (reaction / texture)	Fly ash characteristics (reaction / B content / maximum rate)	Detrimental effects	Ref.
		Pot experiments		
Barley		Relatively low / 50% v/v	B toxicity symptoms / elevated plant B (at ash rate ≥ 12.5% v/v)	64
Barley	Almost neutral / medium	Strongly alkaline / relatively high / 75% v/v	Yield reduction (at ash rate ≥ 50% v/v) / B toxicity symptoms / elevated plant B (at ash rate ≥ 6.25% v/v)	73
Barley, brittlebush (*Encelia farinose*)	Acid / medium Calcareous / medium	Alkaline / high / 8% w/w	Probably B toxicity symptoms / elevated plant and soil B	51
Corn	Acid / medium Acid / light	Alkaline / high / 10% w/w	B toxicity symptoms / elevated plant and soil B (at ash rate ≥ 0.6% w/w)	53
Corn	Acid / light	Alkaline / high / 40% w/w	B toxicity symptoms / elevated plant and soil B (at ash rate ≥ 20% w/w)	74
Corn	Strongly acid / medium	Strongly alkaline / high / 25% w/w	Elevated plant B (at ash rate ≥ 1% w/w)	75
Soybean		10% w/w	Elevated plant B	76
Tomato	Slightly acid	Alkaline / high / 90% v/v	Excessive plant B at ash rate (>50% v/v)	77
Wheat	Strongly acid / heavy	Alkaline / high / 167 Mg ha^{-1} (≅8.35% w/w)	Elevated soil B	43
Alfalfa, Bermuda grass, white clover	Acid Calcareous	Alkaline / 8% w/w	White clover yield reduction / elevated plant and soil B	34
Alfalfa, barley, Bermuda grass (*Cynodon dactylon*), brittlebush, lettuce, Swiss chard, white clover	Acid Calcareous	8% w/w	Lettuce yield reduction	3
French beans, Rhodes grass		70% w/w	Yield reduction for French beans (at ash rate ≥ 30% w/w) and Rhodes grass (at ash rate 70% w/w) / B toxicity symptoms	10
Alfalfa, corn, soybean, wheat	Strongly acid / heavy	Alkaline / high / 167 Mg ha^{-1} (≅8.35% w/w)	Yield reduction / B toxicity symptoms for corn and soybean / elevated plant and soil B (at ash rate > 110 Mg ha^{-1})	78
		Field experiments		
Centipedegrass (*Eremochloa ophiroides*)	Acid / medium	Alkaline / relatively low / 1120 Mg ha^{-1}	Poor initial plant establishment / elevated plant and soil B	79, 80
Corn	Acid / medium	Alkaline / 144 Mg ha^{-1}	Toxicity symptoms (at ash rate ≥ 96 Mg ha^{-1})	81
Alfalfa, timothy, oat	Slightly acid / medium	Acid / high / 700 Mg ha^{-1}	Reduced yield (at ash rate ≥ 400 Mg ha^{-1}) / toxic plant B uptake	72

TABLE 1.3
Cases of Beneficial Effects of Fly Ash on Plant Growth with Respect to B

Plant species	Soil characteristics (reaction / texture)	Fly ash characteristics (reaction / B content / maximum rate)	Increases	Ref.
	Pot experiments			
Alfalfa	Acid / medium	Alkaline / high / 5% w/w	Plant B uptake	22, 23
Alfalfa	Acid	Alkaline / 3.2% w/w (≅80 Mg ha^{-1})	Growth / soil B / plant B	12
Ryegrass	Strongly alkaline	Acid / 8% w/w	Growth / plant B	83
Ryegrass	Acid / medium	Alkaline / low / 5% w/w	Growth / plant B uptake	13
Tomato (*Lycopersicon esculentum*)	Acid	Alkaline / high / 50% v/v	Yield / plant B / soil B	77
Vegetables, millet (*Echinochloa crusgalli*)	Acid / medium	Acid / 10% w/w	Plant B uptake	84
	Neutral / medium	Acid / 10% w/w	Plant B uptake	85
	Field experiments			
Alfalfa	Slightly alkaline	Acid / high / 3.4 kg B ha^{-1}	Yield / plant B uptake	25
	Slightly alkaline	Alkaline / high / 3.4 kg B ha^{-1}		
Corn	Acid / medium	Alkaline / low / 144 Mg ha^{-1}	Soil B / plant B	44
	Acid / light			
Corn	Acid / medium	Alkaline / 144 Mg ha^{-1}		81
Couch grass (*Cynodon dactylon*)	Acid / light	Acid / low / 20% w/w	Root growth / plant B	86
Garlic (*Allium sativum*)	Acid	Alkaline / 825 g B ha^{-1}	Yield	87
Alfalfa, bird's foot trefoil, brome (*Bromus*), orchard grass, timothy	Acid / medium	Acid / low / 5% w/w (≅112.5 Mg ha^{-1})	Plant B	88
Alfalfa, bird's foot trefoil, brome, corn, millet, orchard grass, sorghum (*Sorghum bicolor*), timothy	Acid	125 Mg ha^{-1} (≅5% w/w)	Plant B	89
Beans, cabbage, carrots (*Daucus carota*), onions (*Illium cepa*), potatoes, tomatoes				
Corn, soybean, wheat	Acid	Alkaline / 50 Mg ha^{-1}	Growth / soil B / plant B	12
Scots pine	Strongly acid	Alkaline / 20 Mg ha^{-1}	Plant B	90

ashes and, in addition, the B-supplying power of the fly ashes was as efficient in providing B to plants as the annual applications of B as borax.

Although the use of alkaline fly ash as a liming agent for acid soils is the common case, the use of acidic fly ash as an alternative to gypsum for amelioration of soils with sodicity problems has also been tested. In a pot experiment with padi followed by wheat, Kumar and Singh [92] applied fly ash to a sandy loam soil with sodicity problems at rates up to 7.5% w/w. They found that available soil and plant B were significantly increased with different fly ash levels, but in all cases remained at levels considered acceptable.

1.4 CONCLUSIONS

Any general conclusion concerning fly ash and its use as a soil amendment must be drawn with caution due to the variability of physicochemical properties of ashes and amended soils. Thus, summarizing, fly ash is expected to be rich in B because B is volatilized during coal combustion and condenses onto fly ash particles. Boron availability from fly ash is usually high due to the concentration of significant amounts of B on the external surfaces of fly ash particles and to the solubility of B species releasing upon contact of fly ash with water. Boron release from fly ash is strongly and inversely related to pH. Leaching of fly ash in conjunction to pH decrease is expected to reduce total and available B significantly.

Upon fly ash application to soils, available B concentration is expected to increase, but the extent of this increase depends mainly on fly ash B content and rate of application, degree of ash weathering, soil texture, and final soil pH. Due to the enhanced availability of fly ash B, soil constituents are not expected to play a significant role in removing and thus substantially reducing B in soil solution after fly ash addition to soils, even in cases of alkaline pH range where B adsorption maximum occurs.

Leaching of fly ash-amended soil is a more effective way in decreasing excess B, due to fly ash application. Soil texture significantly affects the time needed for effective leaching. Coarsely textured soils are leached more readily than finely textured soils. From a practical approach, in order to avoid the risk of B phytotoxicity, the use of adequately weathered fly ash rather than unweathered and adequate leaching of amended soil in conjunction with the cultivation of plant species tolerant to B could be suggested. Of course, all the preceding points depend significantly on fly ash B content and rate of application. As far as ash application rate is concerned, in general, fly ashes with high B content must be incorporated into the soils at low rates and vice versa.

ACKNOWLEDGMENTS

The help of Professor V.Z. Keramidas in editing this chapter is greatly appreciated.

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