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Fly ash application on two acid soils and its effect on soil salinity, pH, B, P and on ryegrass growth and composition

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Abstract

Application of alkaline fly ash to acid soils is related to beneficial effects, such as increase of pH to a desired level and nutrient supply to plants, and to possible adverse effects, such as enrichment of soils with substances toxic to plants and animals (e.g. B, Mo, Se) and increase of salinity to undesirable levels. Therefore, use of alkaline fly ash as a beneficial amendment of acid soils needs to be evaluated with respect to phytotoxic and environmental impacts. Samples of alkaline fly ash, from two different sources, were added to two Red Mediterranean acid soils at rates equal to 5, 20 and 50 g kg^{-1} soil, and changes, relative to the untreated soil, of soil pH, salinity, B and P levels were measured. Ryegrass (*Lolium perenne* L.) was grown in pots containing fly ash–soil mixtures for 300 days, and dry biomass yield and cumulative plant uptake of B and P were calculated. Soil application of fly ash at these rates increased the pH, up to about 8, and the electrical conductivity of the saturation extract, up to about 2.5 dS m^{-1}, in both soils. Available soil P (0.5 M $NaHCO_3$ extractable) was unaffected by fly ash application. Water soluble B remained less than 1 mg $litre^{-1}$ in the saturation extract, and hot water extractable B was less than 1 mg kg^{-1} soil. Dry biomass yield of ryegrass and cumulative plant uptake of B and P increased significantly with fly ash application. Therefore, fly ashes with low B and salt content can be used as liming agents in acid soils at rates not exceeding the 40 Mg/ha. Potential environmental impacts must also considered.

Keywords: Acid soils; Electrical conductivity; Fly ash; Soil boron; Red Mediterranean soils

1. Introduction

A considerable part of the electric power in many countries is produced from power stations which utilize lignite coal as fuel. Fly ash is the residue from the combustion of lignite, which enters the flue gas stream and is captured by emission control devices. The ash is subsequently removed, transported, and deposited in open storage areas where it accumulates in large amounts, thus creating the problem of its disposal. The use of fly ash as a soil amendment might be a solution to its disposal, provided that environmental and phytotoxic impacts are minimized.

Chemically, fly ash is a ferro-alumino-silicate mineral, containing substantial amounts of Ca, K, and Na and negligible amounts of C and N (Carlson and Adriano, 1993). Other nutrients usually present in fly ash are P and B and some trace elements (Cu, Zn, Mn, Mo, Se), and radioisotopes that are undesirable for animals and humans (Furr et al., 1978). Fly ash can be extremely acidic (pH 3–4) but usually is extremely alkaline (pH 10–12) because of hydroxides and carbonate salts of Ca and Mg. Also, its soluble salt content is usually high, and the values of the electrical conductivity of the saturation extract (EC_{se}) may vary from 0.63 to 55 dS m^{-1} (Aitken et al., 1984). Physically, fly ash consists of silt-sized particles, is characterized by moderate to extremely high water-holding capacity, and possesses cementing properties to a varying degree. The cementing effects of fly ash possibly could impede root development in certain soils after heavy application of fly ash (Carlson and Adriano, 1993). Otherwise, the presence of fly ash is not expected to deteriorate the physical properties of soils and may even improve some soils remarkably (El-Mogazi et al., 1988).

The agronomic utilization of fly ash might be beneficial, and several studies have shown that it can improve soil structure and water-holding capacity (Chang et al., 1977), enhance soil fertility (Elseewi et al.,

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1980; Ghodrati et al., 1995), and increase the pH of acid soils (El-Mogazi et al., 1988). On the other hand, it may also result in adverse effects on plants, due to B phytotoxicity (Aitken and Bell, 1985; Kukier et al., 1994) and on animals grazing on pastures that have received fly ash, due to Mo and Se toxicities (Furr et al., 1978; Salé et al., 1996). Plant deficiencies of Zn (Mulford and Martens, 1971), P (Page et al., 1979), and Mn (Carlson and Adriano, 1993) have been reported also in fly ash amended soils and attributed to lower availabilities of these elements because of the increase of soil pH. Therefore, as long as soil pH is kept within acceptable limits, acid agricultural soils present a reasonable choice as disposal sites of alkaline fly ash.

In this case, however, use of fly ash as a soil amendment must take into account the properties of fly ash and of soils, if adverse plant and environmental impacts are to be avoided. The objective of this study was to evaluate the effects of soil application of aged alkaline fly ash, derived from two different electric power plants in northern Greece, on: (1) the pH, salinity, available B and P levels of two Red Mediterranean acid soils and (2) the growth and total uptake of B and P by ryegrass (*Lolium perenne* L.) grown in pots containing fly ash–soil mixtures.

2. Materials and methods

Surface soils (0–30 cm) were collected from two locations in northern Greece. The soils, designated as Soil 1 and Soil 2, were under continuous cultivation with wheat and differed in pH (Soil 1, pH = 4.7 and Soil 2, pH = 5.8) and in other physicochemical properties (Table 1). The lower clay content of Soil 1 implies a lower buffering capacity, with respect to pH, than Soil 2. The soils also differed in the mineralogy of the clay fraction with illite and kaolinite prevailing in Soil 1, while illite and smectite were the dominant clay minerals in Soil 2 (Table 1). Soil 1 was classified as Ultic Haploxeralf and Soil 2 as Typic Haploxeralf (Table 1) and both are known widely as Red Mediterranean soils. The soil samples were air-dried and then passed through a 6.35-mm sieve. A part of this material passed through a 2-mm sieve and was used for analysis, and the rest was used for the pot experiment, after mixing it with fly ash.

Table 1
Some physicochemical characteristics of the two soils

	Soil	
	1 (Ultic Haploxeralf[a])	2 (Typic Haploxeralf[a])
pH (1:2 H_2O)	4.7	5.8
pH (1:2 $CaCl_2$)	3.7	4.7
Organic C (g kg^{-1})	6.2	6.9
Sand (%)	63.2	58.6
Silt (%)	21.0	15.2
Clay (%)	15.8	26.2
EC_{se} (dS m^{-1})	0.5	0.5
B in the saturation extract (mg l^{-1})	0.3	0.3
Hot water extractable B (mg kg^{-1})	0.3	0.4
Olsen P (mg kg^{-1})	24.8	47.4
Mineralogy of the clay fraction	Ill, Ka[b]	Ill, Sm[b]

[a] Soil Survey Staff (1996).
[b] Ill, illite; Ka, kaolinite; Sm, smectite.

Two samples of alkaline fly ash (50 kg each) were collected from the electrostatic precipitators of two lignite-fired electric power plants, operating in two different locations in northern Greece. The fly ashes will be designated as Fly ash I and Fly ash II, henceforth. The samples were artificially aged for 6 months, by maintaining them in the open air and leaching periodically with distilled water. This treatment was an attempt to simulate actual conditions in which fly ash, after its collection from the electrostatic filters, is transported to open storage areas where it remains exposed to atmospheric conditions prior its use for any purpose. After aging, the ashes were air-dried and passed through a 2-mm sieve. This material was used for the analytical determinations and for addition to soils.

Inorganic phases predominant in both fly ashes were identified by obtaining X-ray diffraction patterns of randomly oriented powder specimens of the material. The diffractograms were obtained using an instrument (Phillips PW 1830) equipped with a graphite crystal monochromator and a Cu target operating at 45 kV–30 mA. The major components of both ashes were hydrous aluminosilicates (ettringite), quartz, calcite, and anhydrite. Neither fly ash contained high amounts of B and P or excessive amounts of soluble salts, as indicated by their EC_{se} (Table 2). Their acid-neutralizing capacities were similar, on the basis of their $CaCO_3$ content (Table 2).

The fly ashes were applied to soils at rates equal to 5, 20 and 50 g kg^{-1} soil. These rates were established by means of a preliminary experiment, where a wide range of fly ash rates were added to the soils and the increase in pH recorded. Rates were chosen that did not increase the soil pH above 8. The fly ash-soil mixtures after

Table 2
Some physicochemical characteristics of the two fly ashes

	Fly ash	
	I	II
pH (1:2 H_2O)	8.9	8.5
$CaCO_3$ (g kg^{-1})	162	122
EC_{se} (dS m^{-1})	2.7	2.5
Hot water extractable B (mg kg^{-1})	3.1	2.8
Olsen P (mg kg^{-1})	16.7	6.3

equilibration at field capacity for 20 days were air-dried and a quantity with particle diameter less than 2 mm was collected and used for analysis. The rest of the material was used for the pot experiment.

The original soils (untreated soils), the fly ashes and the fly ash–soil mixtures (treated soils) were assayed for their physicochemical characteristics. All analyses were run in duplicate, and average values are reported. Electrical conductivity and water-soluble Ca, Mg, and B were measured in the saturation extract. Hot water extractable B (available soil B) was also measured, and the analytical determination of B was performed by the azomethine-H method (John et al., 1975). Ca and Mg were determined by atomic absorption spectrophotometry. The pH was measured in water and 0.01 M $CaCl_2$ solution at a 1:2 soil to solution ratio. Available soil P was extracted by the Olsen et al. (1954) procedure and determined by the molybdenum blue ascorbic acid method (Olsen and Sommers, 1982). Organic C was determined by wet oxidation (Walkley and Black, 1934), $CaCO_3$ with a volumetric calcimeter (Allison and Moodie, 1965), and particle-size analysis of soils was performed by the hydrometer method (Bouyoukos, 1962).

2.1. Greenhouse pot experiment

One kilogram of the treated or untreated soils was placed in 1-litre plastic pots contained in plastic dishes (15 cm wide and 5 cm deep). Each pot was sown with 0.5 g of ryegrass seeds. The treatments [two soils× two ashes from different locations×four levels of ash application (0, 5, 20, and 50 g kg^{-1})] were replicated three times, and all pots were placed on benches in the greenhouse in a completely randomized design. Randomization was repeated every 15 days. The experiment started the second week of April and lasted for 300 days. Plants were grown under natural lighting conditions in the greenhouse at $22 \pm 3°C$. Frequent aeration, supported by the cooling system of the greenhouse, was provided during the summer months to keep the temperature at the desired level. All pots were watered to field capacity for the first 15 days by subirrigating with distilled water. After that time, subirrigation to field capacity was repeated when the water content of the experimental samples approached the wilting percentage. When salt appeared on the surface of some soils or the surface tended to become dry, surface water (50 ml per pot) was applied. Twenty days after seeding, each pot was fertilized with 100 mg of N and 60 mg of K, as NH_4NO_3 and KNO_3. The micronutrients Cu, Zn, Fe and Mn, were added in amounts equal to 2, 5, 5, and 15 mg per pot, respectively. The N and K fertilization was repeated after each harvest of ryegrass.

Aboveground biomass from each pot (cut at about 2 cm above the surface of the soils) was harvested at approximately 60-day intervals (a total of five harvests), dried at 65°C for 48 h, weighed, and ground to pass a 0.2-mm sieve. Duplicate 0.5-g sub-samples were used for B and P analysis. The sub-samples were ashed at 550°C for 6 h; the ash was dissolved in 10 ml of 0.1 N HCl, filtered, and a portion of the filtrate was used for B and P determination. Tissue concentrations and biomass dry weight were used to calculate plant uptake of B and P per pot for each harvest. At the end of the experiment, the roots were separated from the soil, dried, weighed, ground, and assayed for B and P. Biomass dry weight and plant uptake of B and P per pot of all aboveground harvests and roots were summed to give total dry biomass yield and cumulative plant uptake of B and P per pot. Multiway factorial analysis of variance was conducted to evaluate main effects and interactions and Duncan's multiple range test was used to detect significant differences among the means within each soil or fly ash. The untreated soil was used as a control for both Fly ash I and Fly ash II treatments.

3. Results and discussion

3.1. Effects of fly ash application on some soil characteristics

Application of fly ash resulted in the expected increase of pH in the two soils. Analysis of variance of the pH in the untreated and treated soils showed that the change of pH depended strongly on ash rates (Table 3). There were also significant differences between soils and fly ashes and a strong, statistically significant interaction ($p \leqslant 0.001$) between soils and ash rates. Because of the similar acid-neutralizing capacities of the fly ashes, the rate of pH increase after fly ash addition depended on the buffering capacity of the soil. Soil 2 with the higher buffering capacity, as indicated by the higher clay content, resisted changes in pH. At the highest fly ash application rate (50 g kg^{-1} soil), pH was increased by 2 units relative to the initial pH in Soil 2, while the same fly ash rate caused an increase of 3 pH units in Soil 1 (Table 3).

EC_{se} also increased considerably following fly ash application. Analysis of variance of EC_{se} in the untreated and treated soils showed similar differences as for pH. The value of EC_{se} reached 2.5 dS m^{-1} at the highest rate (Table 3). This value, although not detrimental to most field crops, may be harmful to other sensitive crops and particularly tree crops (Bresler et al., 1982). The increase in EC_{se} was accompanied by an increase of water soluble Ca and Mg, which is in agreement with previous findings (Page et al., 1979; Elseewi et al., 1980).

The liming properties of fly ashes, because of their dependence on the nature of the material and the

Table 3
Average pH and EC_{se} of the soils and the fly ash–soil mixtures

	Fly ash rate (g kg^{-1} soil)			
	0	5	20	50
	pH			
Soil 1				
Fly ash I	4.7 d [a]	5.4 c	7.5 b	7.7 a
Fly ash II	4.7 d	5.3 c	7.4 b	7.7 a
Soil 2				
Fly ash I	5.8 d	6.5 c	7.6 b	7.7 ab
Fly ash II	5.8 d	6.3 c	7.5 b	7.8 a
	EC_{se} (dS m^{-1})			
Soil 1				
Fly ash I	0.5 c	1.6 b	2.5 a	2.4 a
Fly ash II	0.5 c	1.1 b	2.4 a	2.5 a
Soil 2				
Fly ash I	0.5 c	1.3 b	2.4 a	2.3 a
Fly ash II	0.5 d	0.8 c	1.8 b	2.4 a

Multiway ANOVA revealed that the change in pH and EC_{se} depended on soils, fly ashes and ash rates and there was also a significant interaction ($p \leqslant 0.001$) between soils and ash rates.

[a] Means followed by the same letter, within the same property and across rows, are not statistically different at $p \leqslant 0.05$, using the Duncan's multiple range test.

properties of the soils, should be determined carefully in conjunction with the concomitant increase in salinity of the soils. Therefore, for fly ashes and soils similar to those used in this study, a rate of 20 g kg^{-1} soil (about 40 Mg ha^{-1}) addition seems appropriate as far as pH and salinity are concerned.

The initial content of available B and P in the two fly ashes was moderately low, and for that reason, fly ash application to soils did not result in appreciable changes in available soil B and P. Concentration of B in the saturation extract, in all treated soils, remained less than 1 mg $litre^{-1}$, and hot water extractable B did not exceed the level of 1 mg kg^{-1} soil. Both boron levels are not toxic to agricultural crops.

3.2. Effects of fly ash application on three biological indices

Total biomass yield significantly increased following fly ash application in both soils. Analysis of variance of the biomass yield from the untreated and treated soils revealed significant differences between rates (Table 4). There was also a strong, statistically significant interaction between soils and rates ($p \leqslant 0.05$) and between ashes and rates ($p \leqslant 0.01$). The highest yield was with Fly ash I added at 50 g kg^{-1} soil, the relative increase being 80% for Soil 1 and 64% for Soil 2. Increased yields in the two soils were apparently the result of pH improvement, particularly for Soil 1 which had an unfavorably low pH for most crops. Similar yield

Table 4
Total dry biomass yield of ryegrass (g per pot) grown in fly ash–soil mixtures and soils

	Fly ash rate (g kg^{-1} soil)			
	0	5	20	50
Soil 1				
Fly ash I	15.8 d[a] ± 0.2[b]	19.8 c ± 0.3	25.0 b ± 0.3	28.5 a ± 0.5
Fly ash II	15.8 c ± 0.2	20.4 b ± 0.2	26.0 a ± 0.4	26.2 a ± 0.6
Soil 2				
Fly ash I	17.3 d ± 0.7	21.0 c ± 0.5	23.3 b ± 0.6	28.3 a ± 0.6
Fly ash II	17.3 c ± 0.7	19.8 b ± 0.3	25.1 a ± 0.2	25.0 a ± 0.5

Multiway ANOVA revealed a significant interaction between soils and ash rates ($p \leqslant 0.05$) and between ashes and rates ($p \leqslant 0.01$).

[a] Means followed by the same letter, across rows, are not statistically different at $p \leqslant 0.05$, using the Duncan's multiple range test.

[b] Standard error of the mean.

increases following addition of alkaline fly ashes to soils have been reported for various plant species (Plank et al., 1975; Elseewi et al., 1980; Khan and Khan, 1996).

Cumulative plant uptake of B and P in the two acid soils increased significantly following fly ash application, and this increase did not depend on the fly ash source, except for B at the highest rate. It depended, however, on soil type and ash rate for both nutrients (Table 5). For B plant accumulation, there was also a statistically significant interaction between soils and rates and between ashes and rates ($p \leqslant 0.001$), as in the case of biomass yield. The relative increase of B and P plant accumulation was more pronounced in Soil 1, whose initial pH, as mentioned earlier, was harmful to most crops. Therefore, addition of a liming agent had a more dramatic effect on biomass yield and uptake of the two nutrients in Soil 1 than in Soil 2.

Increased B and P accumulation, without a corresponding increase of available soil B and P, can be attributed to better root development in the fly ash treated soils. Root dry weights of ryegrass grown in fly ash–soil mixtures at the two highest rates were significantly greater than that of the control (Table 6). Also, a gradual release of P and especially B from forms that exist in the fly ashes cannot be excluded. These forms are not solubilized by the conventional extractants, used to measure available forms (hot water), but can slowly release their constituents after incorporation into the soil (Kukier and Sumner, 1996).

Boron concentration in the aboveground biomass of the treated soils ranged between 10 and 90 mg kg^{-1} of dry weight, whereas that of the untreated soils ranged between 10 and 60 mg kg^{-1} (Table 7). If a B concentration in plant shoots of 200 mg kg^{-1} is considered the threshold of toxicity (Bradford, 1966), the B levels in aboveground biomass of ryegrass plants indicated no danger of B toxicity in the treated soils. Several cases have been reported where alkaline fly ash addition

Table 5
Cumulative B and P plant uptake by ryegass (mg per pot) grown in fly ash–soil mixtures and soils

	Fly ash rate (g kg^{-1} soil)			
	0	5	20	50
	B uptake			
Soil 1				
Fly ash I	0.46 d[a] ± 0.02[b]	0.68 c ± 0.02	0.94 b ± 0.02	1.56 a ± 0.03
Fly ash II	0.46 c ± 0.02	0.61 b ± 0.01	0.87 a ± 0.01	0.96 a ± 0.01
Soil 2				
Fly ash I	0.55 d ± 0.01	0.71 c ± 0.03	0.85 b ± 0.02	1.26 a ± 0.04
Fly ash II	0.55 c ± 0.01	0.62 b ± 0.01	0.78 a ± 0.02	0.85 a ± 0.01
	P uptake			
Soil 1				
Fly ash I	23.9 c ± 0.9	30.6 b ± 0.5	34.9 ab ± 0.5	35.4 a ± 1.6
Fly ash II	23.9 c ± 0.9	31.7 b ± 0.5	37.7 a ± 0.1	33.0 ab ± 0.8
Soil 2				
Fly ash I	47.0 c ± 1.2	52.5 ab ± 0.8	56.4 a ± 0.7	56.0 a ± 1.1
Fly ash II	47.0 c ± 1.2	50.6 bc ± 0.9	56.5 a ± 0.1	52.9 ab ± 1.1

Multiway ANOVA revealed no difference between fly ashes but there was a difference between soils and ash rates. Especially for B uptake, there was a significant interaction ($p \leqslant 0.001$) between soils and rates and between ashes and rates.

[a] Means followed by the same letter, within the same element uptake and across rows, are not statistically different at $p \leqslant 0.05$, using the Duncan's multiple range test.

[b] Standard error of the mean.

Table 6
Root dry weight of ryegrass (g per pot) grown in fly ash–soil mixtures and soils

	Fly ash rate (g kg^{-1} soil)			
	0	5	20	50
Soil 1				
Fly ash I	3.3 c[a] ± 0.12[b]	3.0 c ± 0.04	5.3 a ± 0.07	5.8 a ± 0.14
Fly ash II	3.3 b ± 0.12	3.2 b ± 0.10	4.8 a ± 0.12	4.9 a ± 0.07
Soil 2				
Fly ash I	1.6 c ± 0.07	2.1 c ± 0.15	3.1 b ± 0.09	4.8 a ± 0.12
Fly ash II	1.6 c ± 0.07	1.9 c ± 0.09	3.3 b ± 0.09	3.9 a ± 0.13

Multiway ANOVA revealed that the increase in root dry weight depended on soils and ash rates.

[a] Means followed by the same letter, within the same row, are not statistically different at $p \leqslant 0.05$, using the Duncan's multiple range test.

[b] Standard error of the mean.

to acid soils (at rates no more than 100 g kg^{-1} soil) resulted in increased B levels in plant tissue (Plank et al., 1975; Page et al., 1979; Kukier and Sumner, 1996) and in certain cases reached toxic levels (Aitken and Bell, 1985; Kukier et al., 1994).

Fly ash of low B and salt content can be used as a liming agent in acid soils, at amounts that depend on the acid-neutralizing capacity of the fly ash and the buffering capacity of the soils. For fly ashes and soils similar to those used in this study, a rate of no more than 20 g kg^{-1} soil, equivalent to 40 Mg ha^{-1}, is considered acceptable. The results of this study also show that the beneficial effects of fly ash addition are reflected in increased nutrient uptake and biomass yield. Boron in fly ash needs special consideration because of its potential toxicity to plants. The final decision for the agronomic use of fly ash must also take into account other factors, such as possible deterioration of soil physical properties for certain soils and potential environmental impacts.

Table 7
Boron concentration (mg kg^{-1}) in the aboveground dry biomass of ryegrass grown in fly–ash soil mixtures and soils

	Fly ash rate (g kg^{-1} soil)			
	0	5	20	50
Soil 1				
Fly ash I	14–47[a]	13–56	11–80	18–88
Fly ash II	14–47	13–48	13–67	15–71
Soil 2				
Fly ash I	10–60	14–62	13–80	16–90
Fly ash II	10–60	13–55	13–64	13–86

[a] Figures represent range over the five cuts.

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