ABSTRACT

A field experiment was conducted to determine the effect of fly ash from a coal combustion electric power facility on soil acidity in a cotton (*Gossypium hirsutum* L.) field. Fresh fly ash was applied to a Bosket fine sandy loam (fine-loamy, mixed, thermic Mollic Hapludalf) soil with an initial soil pH<sub>sal</sub> of 4.8. The fly ash was equivalent to 42 g kg<sup>-1</sup> calcium carbonate with 97% passing through a 60 mesh (U.S. standard) sieve. Fly ash was applied one day before cotton planting in 1999 at 0, 3.4, 6.7, and 10.1 Mg ha<sup>-1</sup>. No fly ash was applied in 2000. Within 60 d of fly ash application in 1999, all rates of fly ash significantly increased soil pH above 6.0. Manganese levels in cotton petioles were reduced significantly by 6.7 and
10.1 Mg ha\(^{-1}\) of fly ash. Soil boron (B) and sodium (Na) concentrations were significantly increased with fly ash. In 1999, B in cotton leaves ranged from 72 to 84 mg kg\(^{-1}\) in plots with fly ash applications. However, no visual symptoms of B toxicity in plants were observed. In 1999, cotton lint yield decreased on average 12 kg ha\(^{-1}\) for each Mg of fly ash applied. In 2000, cotton yields were significantly greater for the residual 3.4 and 6.7 Mg fly ash ha\(^{-1}\) plots than the untreated check. Due to the adverse yield effects measured in the first year following application, fly ash would not be a suitable soil amendment for cotton on this soil at this time.

### INTRODUCTION

Industrial electric power facilities consume three-fourths of the coal mined in the USA, and disposing of the combustion waste from these facilities has become a serious problem. The USEPA estimates that more than 110 million Mg of combustion waste is produced each year by coal-fired power facilities (USEPA, 1988). Fly ash and bottom ash account for 90% of all power facility combustion waste. Fly ash is the portion of the combustion residue that enters the flue gas stream in power-generating facilities. Davison et al. (1974) reported that fly ash consists of many small, glass-like particles, which range in size from 0.01 to 100 \(\mu\)m. The reported specific gravity of fly ash ranges was from 2.1 to 2.6 (Bern, 1976).

A survey by the American Coal Ash Association (2002) showed that the largest commercial use for fly ash is in the cement, concrete, and grout industries. Fly ash is also an important material in structural and road base fills. Unfortunately, approximately 62% of the fly ash produced each year by electric power facilities is not used. Most of this fly ash is stockpiled in sediment ponds with rubber liners to prevent compounds in the fly ash from leaching into ground water.

Excessive carbon in fly ash is the main obstacle to finding more commercial uses for fly ash. Carbon contents in fly ash above 6% are not suitable for direct use in concrete because of interactions between the carbon and the chemical admixtures used in concrete. Most concrete companies prefer fly ash with less than 1% carbon. The amount of carbon in fly ash is greatly affected by the design of boilers in a facility and type of coal burned. Many power facilities in the USA use wall-fired units burning low-S western U.S. subbituminous coal. A typical Wyoming Power River Basin Coal (Wyodak) contains 0.63% S as compared with a typical Illinois coal (Illinois #6), which contains 4.82% S (McClurg, 2002). Low-S coal is often burned to comply with USEPA sulfur dioxide gas emissions standards. The USEPA developed the sulfur and nitrogen gas emission standards for power facilities to achieve the goals of the U.S. Clean Air Act of 1970.

Research in Kentucky by Hower et al. (1999) found that using low NO\(_x\) combustion combined with burning low-S coal resulted in unmarketable fly ash because of high carbon contents. The combustion of low-S coal often produces amounts and forms of carbon in the fly ash that make it unacceptable in concrete, cement, and grout production.
The suitability of fly ash for concrete has been further reduced by the widespread use of ammonia injection by power facilities to decrease NO\textsubscript{x} emissions. This process has been applied in selective catalytic reduction and selective noncatalytic flue gas treatment systems to meet more stringent NO\textsubscript{x} standards that cannot be met solely by low NO\textsubscript{x} burners. Removal of part of the added ammonia is often required to make the ash suitable for concrete applications. This has added more cost to handling of fly ash and producing electricity.

Carbon removal from fly ash is a new area of research that could help fly ash disposal problems. Baltrus et al. (2001) studied unburned carbon concentrates from fly ash produced from burning bituminous coal. The fly ash carbon was reported to have properties similar to most carbon blacks. The untreated carbon extracted from the fly ash was found to be a marketable substitute for carbon black provided if it could be obtained in sufficient purity. The principal uses of carbon black are as a reinforcing agent in rubber compounds (especially tires) and as a black pigment in printing inks, surface coatings, paper, and plastics. A new proprietary technology called Carbon Burn-Out is also being studied as a means of reducing carbon in fly ash (Keppeler, 2001).

Other uses such as liming low-pH agricultural soils are needed by the power industry to help dispose of fly ash. In 2001, only 186,16 Mg of the fly ash produced by electric power facilities was used in agriculture (American Coal Ash Association, 2002).

Fly ash may be useful as a soil amendment for crop production (Sims et al., 1995). Chapman (1984) determined that 3.6 to 5.4 Mg of fly ash was equivalent to 1.8 Mg of agricultural lime in raising soil pH on three silt loam soils. Transporting agricultural lime from quarries to cotton fields is a major expense for farmers in the Mid-South region of the USA. Lime ranges in costs from $7 to $25 per Mg depending on how far it has to be transported. Soil test results showed that 26% of the samples sent to the University of Missouri Soil Test Laboratories in 1997 had soil pH values less than 5.4 and needed lime to correct the acidity (M. Nathan, personal communication, 1998). No limestone quarries are located in the cotton-producing counties of southeastern Missouri. However, fly ash is available free of charge from a cyclone-fired power facility at New Madrid, MO. The New Madrid facility burns Wyoming low-S subbituminous coal from Power River basin to meet USEPA emissions standards. The fly ash from the facility ranges from 9 to 22% C, which is too high for the concrete industry.

Adriano et al. (1978) determined that K, Ca, and Mg levels in tissue of forage and vegetable crops grown in fly ash-amended soil were not increased consistently by fly ash applications. In a review of fly ash literature, Adriano et al. (1980) reported that levels of S, Mo, and B were significantly greater in forage plants grown in fly ash-amended soil compared with plants from untreated controls. The concentrations of Al, Se, Sr, As, Ba, Cs, Rb, W, and V were also greater due to fly ash treatments. This indicates that growing crops may potentially be used as a method for scavenging heavy metals.

Fary et al. (1990) found that B is concentrated on the surfaces of fly ash particle as soluble salts and oxides, which are readily dissolved. Kukier and Sumner (1996) found that excessive rates of fly ash increased B in corn (Zea mays L.) tissue to toxicity levels.
Oertli and Roth (1969) reported that cotton was more tolerant to high B levels than soybean \textit{[Glycine max (L.) Merr.]. Cotton is a crop to which farmers in the southeastern USA often apply soil or foliar B fertilizer to avoid B deficiency. The B sufficiency range cited by Plank (1982) for upper leaves from cotton plants collected from first square to first bloom was 20 to 60 mg B kg\(^{-1}\). Mills and Jones (1996) reported the same B tissue sufficiency range (20 to 60 mg kg\(^{-1}\)) for cotton petioles at full bloom. In field tests in Louisiana, Miley et al. (1969) reported that cotton plants at first square were deficient in B when petiole concentrations were 16.4 mg B kg\(^{-1}\) and leaf blade concentrations were 15.6 mg B kg\(^{-1}\).

Very little research on B toxicity in cotton has been reported in the literature. Bresler et al. (1982) proposed that the adverse effects of salts in plants can be divided into three categories: osmotic or total salt effects, specific-ion effects, and secondary specific-ion effect. Plank (1982) reported that B toxicity in cotton can occur when the B tissue level in young leaves exceeds 25 mg B kg\(^{-1}\). Oertli and Roth (1969) reported that dry matter yields decreased when cotton plants were grown in solutions containing greater than 10 mg B kg\(^{-1}\). Visual phytotoxic B symptoms in cotton were leaf cuppy, chlororis, and necrosis.

In 1999, an agronomic research project was begun to determine whether fly ash can be used as a substitute for lime on cotton fields, and if it can be used, what fly ash application rate is appropriate.

### MATERIALS AND METHODS

A 2-yr cotton experiment was conducted on a Bosket fine sandy loam soil at the University of Missouri-Delta Center Rhodes Farm (36°24' N, 89°54' W) in Dunklin County, Missouri in 1999 and 2000. Initial soil test results showed the plots ranged from 4.7 to 4.9 pH\(_{\text{salt}}\) (in 0.01 \(M\) CaCl\(_2\); Woodruff, 1948), 3.0 cmol kg\(^{-1}\) soil neutralizable acidity (Woodruff, 1948), and 5.2 cmol kg\(^{-1}\) soil cation exchange capacity (Thomas, 1982).

The University of Missouri lime recommendation for this soil was to apply 1120 kg ha\(^{-1}\) of effective neutralizing material (ENM) to bring the soil pH to 6.1. In Missouri, ENM is used to indicate the effectiveness of liming materials based on measured calcium carbonate equivalent and the amount of material passing through three sieve sizes (Missouri Liming Material Standards, 1999). The fly ash used in the test was obtained fresh from the Associated Electric Cooperative Incorporated Power Plant at New Madrid, MO. The fly ash was tested for its ENM value by the University of Missouri Experiment Station Chemical Laboratory, Fertilizer Section (Columbia, MO). The material was very fine with 97.1% of it passing a 60 mesh (U.S. standard) sieve. The neutralizing capacity of the fly ash was 0.163 kg ENM kg\(^{-1}\) (41.8 g kg\(^{-1}\) calcium carbonate equivalent). Multiplying the liming recommendation from the buffered pH of the soil by the liming ENM resulted in a lime recommendation of 6.7 Mg ha\(^{-1}\) of fly ash. Boron content in the fly ash was determined by the hot water-soluble method (Bingham, 1982). The fly ash was also tested for 18 other elements by aqua regia digestion with inductively coupled plasma–atomic emission spectroscopy (ICP–AES) determination (Dalquist and Knoll, 1978). The following elements...
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were tested: Al, As, B, Ca, Cd, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Se, and Zn.

Three fly ash rates were compared with an untreated control in a field experiment. Fly ash treatments were 3.4 Mg ha\(^{-1}\) (50% recommended ENM), 6.7 Mg ha\(^{-1}\) (100% recommended ENM), and 10.1 Mg ha\(^{-1}\) (150% recommended ENM). Fly ash was applied one day before cotton planting in 1999. No fly ash was applied in 2000. The material was broadcast by hand and incorporated with a disk to a depth of approximately 15 cm. Each treatment was replicated four times in a randomized complete block design. Plots were 9.2 m long and four 97-cm rows (3.9 m) wide. Stoneville cultivar BXN 47 was planted into these plots on 13 May 1999 and 15 May 2000. Ammonium nitrate was broadcast (100 kg N ha\(^{-1}\)) at first square growth stage each year. The center two rows of each plot were mechanically harvested for yield on 15 Oct. 1999 and 21 Oct. 2000. Plots were not irrigated.

Soil samples were collected from the 0- to 15-cm depth each month from planting through harvest. Samples were analyzed for soil pH, electrical conductivity (EC), and B, S, and Na content. Soil samples were also collected from each plot in November each year from the 0- to 30-, 30- to 60-, and 60- to 90-cm depths. These samples were analyzed by ICP–AES for the content of the 18 elements as measured in the fly ash. Samples were also analyzed for diethylene triamine pentaacetic acid (DTPA)-extractable Mn (Gambrell and Patrick, 1982). Cotton petiole and leaf blade samples were collected from the fourth fully expanded leaf from the top of cotton plants in each plot at 2 wk following first bloom. Samples were analyzed by ICP–AES (Munter et al., 1984) for the content of the same elements as measured in the fly ash and soil.

Statistical analyses of the data were performed with SAS Institute (1990) using the analysis of variance and regression procedures. Fisher's protected least significant difference (LSD) was calculated at the 0.05 probability level for making treatment mean comparisons.

### RESULTS AND DISCUSSION

All fly ash treatments significantly increased soil pH compared with the untreated check in 1999, the first year after application (Fig. 1). Generally, higher fly ash rates resulted in higher soil pH. The recommended rate of fly ash (6.7 Mg ha\(^{-1}\)) increased the soil pH above 6.1. Soil pH values were similar for the 6.7 and 10.1 Mg ha\(^{-1}\) rates. The pH did not change significantly from November 1999 to November 2000. In November 2000, plots that received 3.4, 6.7, and 10.1 Mg ha\(^{-1}\) fly ash applications in 1999 had average soil pH values of 5.7, 6.3, and 6.7, respectively. The soil pH in the untreated check plots averaged 4.9.

Fig. 1. Effect of four rates of fly ash applied before cotton planting on pH in the upper-15-cm soil layer of a Bosket fine sandy loam soil in 1999.
The primary effect of soil pH on plant growth, within the range of 4 to 10, is not the H⁺ or OH⁻ activities per se but the associated chemical environments (Foth and Ellis, 1997). Phytotoxic levels of soluble Al and Mn are a potential problem in soils with pH values below 5.5. By increasing soil pH, fly ash treatments decreased Mn availability in the soil. The effect of fly ash on reducing extractable Mn in the soil was significant in the 0- to 30-cm depth (Fig. 2). Soil DTPA-extractable manganese levels were 18 to 34% lower for the ash treatments than the untreated check. Fly ash also significantly reduced the cotton petiole levels of Mn (Table 1).

In 1992, the USEPA released the National Sewage Sludge Rule developed under the national Clean Water Act. For land application, the general rule is to apply the sewage sludge at an "agronomic rate" consistent with crop needs. Trace elements in all fly ash treatments applied in 1999 were well below USEPA (1992b) annual loading rates for soil applied sludge (Table 2). Cumulative loading rates define the total length of time a site can receive sewage sludge (Pierzynski et al., 1994). If adequate lime is applied to raise soil pH to 6.5 or above, farmers usually do not need to apply more lime for 3 to 5 yr. Because fly ash usually contains higher concentrations of aromatic hydrocarbons than sludge, environmental standards developed for sludge may not be adequate for land-applied fly ash. Although B
and Na are not hazardous pollutants, we were concerned that they might reduce cotton growth. The fly ash contained 907 mg kg\(^{-1}\) hot water–soluble B and 4.67 g kg\(^{-1}\) Na.

**View this table:** Table 2. Concentrations and total amounts applied of trace elements from fly ash applications made in 1999 as compared with annual maximum load rates for sewage sludge established by the USEPA in 1992.

Soil electrical conductivity (EC) was not significantly increased by fly ash applications (Table 3). The highest EC values measured in fly ash plots averaged only 0.02 S m\(^{-1}\). This is much lower than the measured EC (0.94 S m\(^{-1}\)) by Pettiy and Switzer (1998) from dead spots in Mississippi cotton fields with high Na. Tissue Na levels at 2 wk after first bloom were increased significantly by fly ash but were not elevated enough to cause osmotic or specific-ion problems in cotton plants (Table 3).

**View this table:** Table 3. Soil electrical conductivity and extractable boron and sodium contents at a 0- to 15-cm depth in 1999 as affected by rates of a single application of fly ash on 12 May 1999 at Clarkton, Missouri.

In 1999 and 2000, soluble B levels in the 0- to 15-cm depth were significantly greater for all fly ash treatments than the untreated check (Table 3). The rate of fly ash applications significantly affected extractable soil B in the 0- to 30-cm depth in 1999 and 2000 (Fig. 3 and 4). Generally, soil B levels declined over time. Cotton leaf and petiole levels of B, Na, and Mg were increased both years in plots treated with fly ash (Table 4).

![Fig. 3. Hot water–soluble boron levels at three soil depths on 11 Nov. 1999 from a Bosket fine sandy loam soil treated with four rates of fly ash before cotton planting.](http://jeq.scijournals.org/cgi/content/full/33/1/343)
No visual symptoms of B toxicity were observed in 1999 or 2000. However, in 1999, leaf B concentrations in fly ash plots collected 2 wk after first bloom were 20 to 40% higher than the upper limit of B sufficiency range cited by Mills and Jones (1996) and Plank (1982). Averaged across fly ash rates in 1999, B in leaves was 39 mg kg\(^{-1}\) higher than B in petiole. This showed that B levels in cotton were very plant-part specific. Tissue levels of B in 2000 were also affected by the previous-year fly ash applications; overall, however, B levels were much lower than in 1999. A general observation was that cotton plants in all plots including untreated check treatments grew 15 to 20 cm taller in 2000 than in 1999.

Unlike several previous research projects in the literature, our soil tests did not indicate that fly ash applications created phytotoxic B soil levels. The highest level of B in 1999 was only 0.93 mg kg\(^{-1}\), which is much less than the toxicity levels in growth solutions for cotton reported by Oertli and Roth (1969). In the 0- to 30-cm soil depth, B was 22% less in 2000 than in 1999. Boron in the 30- to 90-cm depth was 6% higher in 2000. This indicates that rainfall may have leached part of the B down the well-drained profile of the Bosket fine sandy loam soil. Winter rainfall from November 1999 to April 2000 was 605 mm. Gangloff et al. (1997) estimated that 1500 mm of rainfall is needed to sufficiently leach B from soil-applied fly ash to produce B concentrations suitable for most crops. In southeastern Missouri (located in National Weather Service Climate Division 6), the 30-yr average annual rainfall was 1220 mm from 1971 to 2000. Kukier and Sumner (1996) found that leaching and weathering of a fly ash under ponding conditions decreased the fly ash B content and B in corn grown on a fly ash-amended soil. Ghodrati et al. (1995) also found that pre-leaching B from fly ash before applying it to soil improved plant growth. Under field conditions Townsend and Gillham (1975) estimated that 2 to 3 yr may be required to reduce the phytotoxic effect of B in fly ash–treated soils. Ciravolo and Adriano (1979) reported that no detectable B toxicity symptoms were reported after fly ash was completely weathered.
Concentrations of Ca, K, and Zn in cotton petioles and leaves were not affected consistently across the two growing seasons (Table 5). Copper, nickel, and phosphorus were detected in petioles but showed no apparent effect from fly ash treatments either year. The following elements were not found in detectable levels in cotton petioles: Al, As, Cd, Cr, Mo, Pb, and Se.

**CONCLUSIONS**

This study showed that fresh fly ash from an electric power facility can be used to increase soil pH in a cotton field that was too acidic for optimum cotton production. However, fly ash treatments reduced cotton yields even at one-half the recommended rate in the first year after application. Applying fly ash to plots with acid soil reduced levels of Mn in the soil and in cotton petioles and leaves. In the first growing season, a linear reduction in cotton yields resulted as the rate of fly ash increased. In the second growing season, a positive yield response to fly ash was found from applying fly ash at the recommended rate. Until it is determined why...
fly ash decreased yields in the first year after application, fly ash cannot be recommended for cotton on southeastern Missouri soils.

Initially we suspected that excessive soil salts (as measured by soil EC) or toxic levels of B caused the cotton yield reductions from fly ash application in the first year. Soil tests showed that B levels in plots with fly ash were less than 1 mg ha\(^{-1}\), which does not exceed the sufficiency range for cotton. However, the B in cotton leaves was 20 to 40% higher than B sufficiency levels reported in the literature. Future research with soil applications of fly ash by the investigators will include analyzing cotton plants for concentrations of anions such as Cl\(^{-}\) or F\(^{-}\) and evaluating carbon compounds in the fly ash that may have inhibited cotton growth and yield.

Hansen and Schaeffer (1995) reported that fluoranthene, naphthalene, phenanthrene, and pyrene were each present in fly ash in concentrations ranging from 2 to 5 mg kg\(^{-1}\). Naphthalene is used directly in moth repellant and insecticides. Whether these polycyclic aromatic hydrocarbons (PAHs) are toxic to cotton in low concentrations has not been tested. Based on no human data and inadequate data from animal bioassays, the USEPA (1992a, 1993) has placed these chemicals in Weight-of-Evidence Group D, not classified as to human carcinogenicity.

Implementing new carbon reduction practices for fly ash will be expensive for power facilities burning low-S coal in cyclone-fired boilers; however, the benefits may be threefold. The fly ash with the carbon removed would be more commercially desirable for concrete additives, and the removed carbon might be marketable for carbon black. Finally, the fly ash may also be more useable as agricultural lime if the removed carbon contains phytotoxic organic compounds.

Unless the carbon levels in fly ash can be reduced or other uses for high carbon ash found, power facilities will have to continue building new sediment ponds to stockpile the fly ash. Generally, stockpiling fly ash in rubber-lined sediment ponds does not pose significant environmental dangers. The greatest environment danger from a sediment pond is that a major earthquake will rupture the rubber liner. Depending on the type of coal burned, fly ash usually contains relatively low concentrations of the trace elements monitored by USEPA for sludge application on soils. The biggest problem with constructing new sediment ponds is that it consumes valuable land resources for generations to come. Therefore, we need to find other methods of disposing of fly ash in the near future.

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