DRY FLUE GAS DESULFURIZATION BYPRODUCTS AS AMENDMENTS FOR ACID AGRICULTURAL SOILS[1]

Richard C. Stehouwer, Paul Sutton, and Warren A. Dick[2]

Abstract: Dry flue gas desulfurization (FGD) byproducts result from the removal of SO_2 from the stack gases of coal-fired boilers and are mixtures of coal fly-ash, $CaSO_4$, and unspent sorbent. Dry FGD byproducts frequently have neutralizing values greater than 50% $CaCO_3$ equivalency and thus have potential for neutralizing acid agricultural soils. Owing to the presence of soluble salts and various trace elements, however, soil application of dry FGD byproducts may have adverse effects on plant growth and soil and water quality. The use of a dry FGD by-product as a limestone substitute was investigated in a field study on three acid agricultural soils (pH 4.6, 4.8, and 5.8) in eastern Ohio. The by-product (60% $CaCO_3$ equivalency) was applied in September, 1992, at rates of 0, 0.5, 1.0, and 2.0 times the lime requirement of the soils, and alfalfa (*Medicago sativa* L.) and corn (*Zea mays* L.) were planted. Soils were sampled in April, 1993 and analyzed for pH and water soluble concentrations of 28 elements. Soil pH was increased by all FGD rates in the zone of incorporation (0-10 cm), with the highest rates giving a pH slightly above 7. At 10- to 20-cm, pH was increased from 4.7 to 5.2 in two soils; there was no effect on pH at 20- to 30-cm. Calcium, Mg, and S increased, and Al, Mn, and Fe decreased with increasing dry FGD application rates. No trace element concentrations were changed by dry FGD application except B which was increased in the zone of incorporation. Dry FGD increased alfalfa yield on the most acidic soil, and decreased corn grain yield on another soil. Application of dry FGD equivalent to the lime requirement of acid soils appears to be beneficial to acid-sensitive crops such as alfalfa. No detrimental effects on soil quality were observed in this study.

Additional Key Words: agricultural lime, beneficial use, coal ash, gypsum, liming, scrubber waste.

Introduction

The 1990 amendments to the Clean Air Act mandate a two-stage, 10-million ton reduction in annual SO_2 emissions in the United States by the year 2000. One strategy for meeting this standard is for utilities to scrub SO_2 from flue gases. Dry flue gas desulfurization (FGD) processes utilize lime-based sorbents in various scrubber vessels and produce highly alkaline byproducts which contain unspent sorbent, coal ash, and the SO_2 reaction product anhydrite ($CaSO_4$). These byproducts are generally disposed of in landfills. Because of limited landfill space and increased tipping fees, the development and demonstration of beneficial and environmentally safe uses for these byproducts would significantly reduce the cost of SO_2 scrubbing.

Because of their alkalinity, one possible beneficial use for these byproducts is as a limestone substitute for amendment of acid agricultural soils. Land application of fluidized bed combustion byproducts (one type of dry FGD byproduct) as a lime substitute and a source of Ca and S has been investigated in a number of studies (Terman et al. 1978, Holmes et al. 1979, Stout et al. 1979, Korcak 1980). These studies have generally reported positive effects on plant growth and crop yield, with negative effects occurring only at application rates of 25 wt % or higher. Most studies with fluidized bed materials have investigated soil pH and plant responses,

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with little emphasis on potential environmental impacts. In this study we have investigated the responses of two crops (alfalfa and corn) grown on three acid agricultural soils amended with a dry FGD byproduct applied at rates based on the liming requirement of the soils. In addition to crop responses, soil chemical effects and transport of the FGD material were monitored.

Materials and Methods

Field studies were conducted on three acid agricultural soils located at Wooster, Coshocton, and Canfield in eastern Ohio. Characteristics of these soils are given in table 1. Dry FGD byproduct was obtained from a pressurized fluidized bed combustion (PFBC) boiler. The PFBC boiler produced two byproduct streams: a coarse, granular bed material, and a much finer, particulate material collected in a primary cyclone (table 2). The PFBC byproduct used in this study was a 40:60 (wt/wt) mixture of the bed and cyclone materials.

The PFBC was applied in September 1992 at rates equivalent to 0, 0.5, 1, and 2 times the lime requirement (LR) of each soil. The soil LR was determined by use of the SMP buffer method (Shoemaker et al. 1962). The amount of calcium carbonate required to raise the soil pH to 7 was divided by the $CaCO_3$ equivalency of the PFBC (0.60) and multiplied by the lime requirement rate treatment factor to arrive at the amount of PFBC applied to each of the three soils (table 3). The PFBC was surface-applied using a lime spreader and then incorporated to a depth of 10 cm with a roto-tiller. Separate plots of each treatment were planted to alfalfa (*Medicago sativa* L.) and corn (*Zea mays* L.). Alfalfa was planted immediately after PFBC incorporation, while corn plots were seeded with a rye (*Secale cereale* L.) cover crop. In the spring the rye cover was killed with glyphosate (*N*-(phosphonomethyl)glycine), and corn was planted in early May. Corn plots were fertilized with N, P, and K, and alfalfa plots with P and K according to soil test and Ohio Agronomy Guide (Ohio Cooperative Extension Service 1990) recommendations.

All PFBC rate and crop treatment combinations were replicated four times at each location, using a randomized complete block experimental design. Corn and alfalfa were run as separate experiments.

Soil samples were collected from all plots at depths of 0 to 10, 10 to 20, and 20 to 30 cm in April 1993. Samples were air-dried, crushed, and passed through a 2-mm sieve. Soil pH was determined in a 1:2 (soil:water, wt/wt) paste, and water extracts were prepared by shaking a 1:10 (soil:water, wt/wt) mixture for 30 min, followed by filtering though a 0.45-μm membrane filter. Water extracts were analyzed for Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sr, V, and Zn by inductively coupled plasma emission spectrophotometry.

Alfalfa was harvested in July and September at the Wooster and Coshocton locations, and in July at the Canfield location. Corn grain was harvested at all three locations in October 1993.

Table 1. Soil characterization of 0 to 20 cm depth of Wooster, Coshocton, and Canfield soils.

Soil	Classification	LR[1], Mg/ha	pH	Bray P_1, mg/kg	Exchangeable, mg/kg			CEC[2], $cmol_c/kg$
					K	Ca	Mg	
Wooster	Aquic Fragiudalf	20.6	4.6	9	103	430	85	15.7
Coshocton	Aqultic Hapludalf	13.7	4.8	9	118	300	87	12.1
Canfield	Typic Fragiudalf	2.8	5.8	29	171	1130	29	8.7

[1] Lime requirement, amount of ag-lime required to raise soil pH to 7.

[2] Cation exchange capacity.

Table 2. Characterization of PFBC byproducts.

Parameter		PFBC, cyclone	PFBC, bed
pH (1:1, water)		10.5	12.2
Calcium carbonate equivalent, %		60.3	60.0
Particle size distribution, %			
>2 mm		0.0	4
2-0.1 mm		0.0	95
100-50 μm		23.5	1
50-2 μm		76.1	0
<2 μm		0.4	0
Major minerals, %			
Dolomite		25	ND[1]
Anhydrite		22	36
Periclase		12	27
Total Chemical Analysis:			
Al	%	3.93	2.75
Ca	%	17.53	24.44
Fe	%	5.17	2.08
K	%	0.53	0.14
Mg	%	10.64	16.28
Si	%	7.24	45.25
S	%	5.21	8.64
As	mg/kg	75.0	46.7
B	mg/kg	169.0	206.0
Cd	mg/kg	1.0	3.5
Cr	mg/kg	36.9	17.5
Cu	mg/kg	35.0	912.9
Pb	mg/kg	24.5	28.0
Coal-ash	%	32.1	10.0

[1] Not detected.

Table 3. Amount of PFBC by-product applied to the Wooster, Coshocton, and Canfield soils at each lime requirement rate factor.

Fraction of LR[1]	Amount of PFBC applied to soil, Mg/ha		
	Wooster	Coshocton	Canfield
0.0	0.0	0.0	0.0
0.5	17.2	11.4	2.4
1.0	34.3	22.8	4.7
2.0	68.6	45.6	9.4

[1] Lime requirement, amount of ag lime required to raise soil pH to 7.

Results

Soil Chemistry

Clearly the PFBC material was effective as a liming material. Soil pH was rapidly raised in the Wooster and Coshocton soils, and the increase was sustained through the winter (fig. 1). In the Canfield soil no effect on pH was seen immediately after incorporation, and the following spring there was only a small increase at the 2xLR rate. Apparently the SMP buffer underestimated the lime requirement of this moderately acid soil, and an insufficient amount of PFBC was applied.

The greatest effects on water soluble concentrations of Ca, Mg, and S occurred in the Wooster and Coshocton soils where the 1xLR rate was equivalent to 34.3 and 22.8 Mg/ha, respectively. In the Canfield soil, where the 1xLR rate was only 4.7 Mg/ha, the effects of PFBC application on Ca, Mg, and S were much less.

The major elements in the PFBC are Ca, S, and Mg (table 2), and in each soil application of PFBC increased the water-soluble levels of these elements. Surface soil concentrations of Ca were increased in each of the soils (fig. 2). Only in the Coshocton soil, however, was there significant downward movement of Ca. Much of the Ca in the PFBC is present as $CaSO_4$, which is much more soluble than $CaCO_3$ and thus more likely to be leached downward. The amount of winter precipitation at the two sites was similar, thus the amount of leaching was likely also similar. The differences in movement of Ca between the Wooster and Coshocton soils may be due to the higher cation exchange capacity and exchangeable acidity of the Wooster

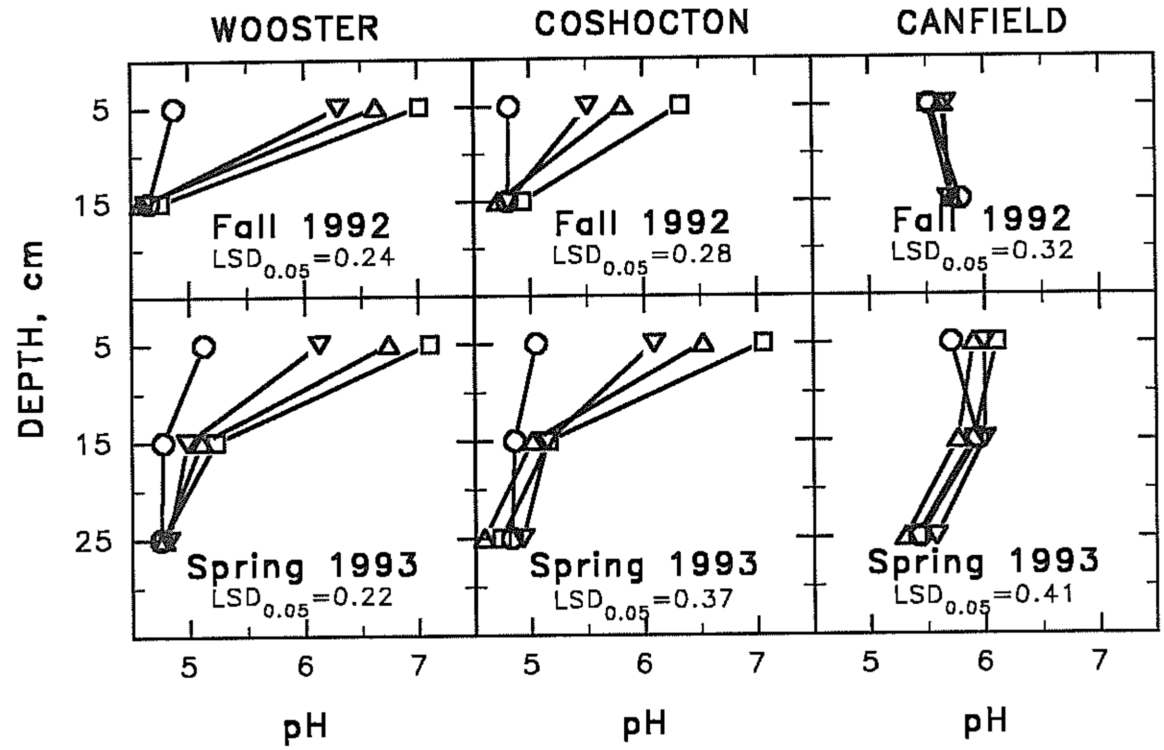

Figure 1. Distribution of pH in Wooster, Coshocton, and Canfield soils in fall and spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ = 1xLR, □ = 2xLR).

soil. Reaction of $CaCO_3$ with exchangeable acidity in the Wooster soil may have led to greater sorption of Ca and, therefore, less movement. The downward movement of Ca during just one winter indicates there is potential for surface application of PFBC to improve the Ca status of soil below the zone of incorporation.

Sulfur is present in PFBC primarily as $CaSO_4$. In column leaching studies with PFBC-amended mine spoil, it was found that greater than 95% of leachate S was present as sulfate (SO_4^{2-}) (Stehouwer et al. 1992). Thus, because of its anionic form, it was expected that S would be highly mobile, as is clearly shown by the elevated S concentrations at all depths in all three soils (fig. 3).

All three soils showed increased water-soluble Mg concentrations at 0-10 cm following PFBC application (fig. 4). Distribution of Mg in the soil profiles was similar at Wooster and Coshocton, with very clear downward movement of Mg below the zone of incorporation. Even though the PFBC contained nearly twice as much Ca as Mg (table 2), movement of Mg on a mass basis was similar to that of Ca in the Coshocton soil, and greater than that of Ca in the Wooster soil. On a mole basis, therefore, movement of Mg was greater than that of Ca. Thus the mobility of the Mg in PFBC appears to be greater than that of the Ca. The same phenomenon was observed in column leaching studies with PFBC, where leachate concentrations of Mg were much higher than those of Ca (Stehouwer et al. 1992). Also, S concentrations in leachates from PFBC-amended spoils were much higher than those from spoil amended with an FGD byproduct containing no Mg. This is due to the much greater solubility of $MgSO_4$ compared with $CaSO_4$ (nearly 300 times more soluble). Movement of Mg relative to Ca was also likely increased by the greater ion selectivity of most soils for Ca relative to Mg (Bohn et al. 1985).

Surface soil concentrations of water-soluble Al, Mn, and Fe, ions which are frequently phytotoxic in acid soils, were decreased by PFBC amendment in all three soils with the exception of Fe in the Coshocton and Canfield soils (figs. 5- 7). This is consistent with the increase in pH that occurred in these soils (fig. 1). The smallest decreases were in the Canfield soil, where the lowest rates were applied, the pH increases were the least, and initial concentrations of Al, Mn, and Fe were the lowest of the three soils. There was no evidence that PFBC decreased concentrations of these elements below the zone of incorporation. On the contrary,

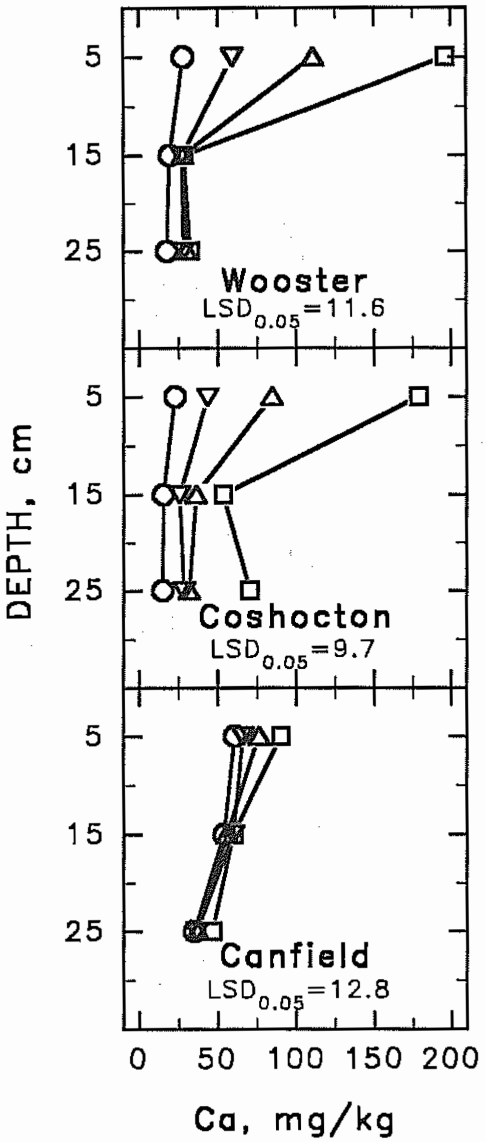

Figure 2. Distribution of water soluble Ca in three soils in the spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ =1xLR, □ = 2xLR).

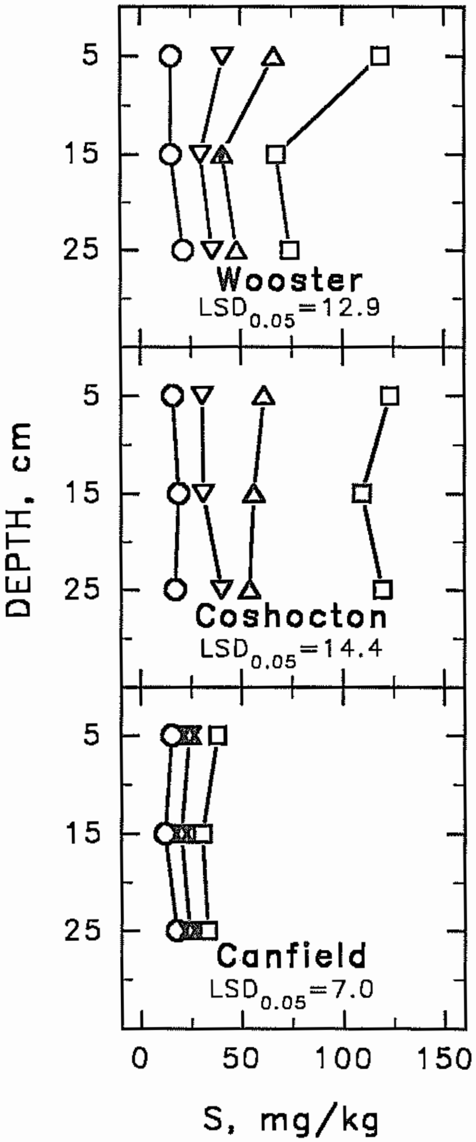

Figure 3. Distribution of water soluble S in three soils in the spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ =1xLR, □ = 2xLR).

particularly for Mn, and less so for Fe, there appeared to be mobilization from the zone of incorporation to underlying soil. The mobilization of Mn appeared to be the result of cation exchange between Mn^{2+} and Ca^{2+} and Mg^{2+}. Availability of Mn transported deeper in the profile would also be increased because of the lower soil pH below 10 cm. Of the trace elements, only B was affected by PFBC amendment (fig. 8). Concentrations of water-soluble B were increased in the zone of PFBC incorporation in all three soils. There was also evidence of downward movement of B in the Coshocton soil, as was observed with Ca, Mg, S, and Mn. The coal fly ash component of the PFBC material is the primary source for the B. Elevated B, or B phytotoxicity, has been reported in several studies involving land application of coal fly ash (Carlson and Adriano, 1993). It should be noted, however, that the water-soluble B concentrations observed in this study were well below phytotoxic levels; indeed, B toxicity was not observed on alfalfa or corn grown on these three PFBC-amended soils.

Water-soluble concentrations of all other measured elements showed no measurable changes in response

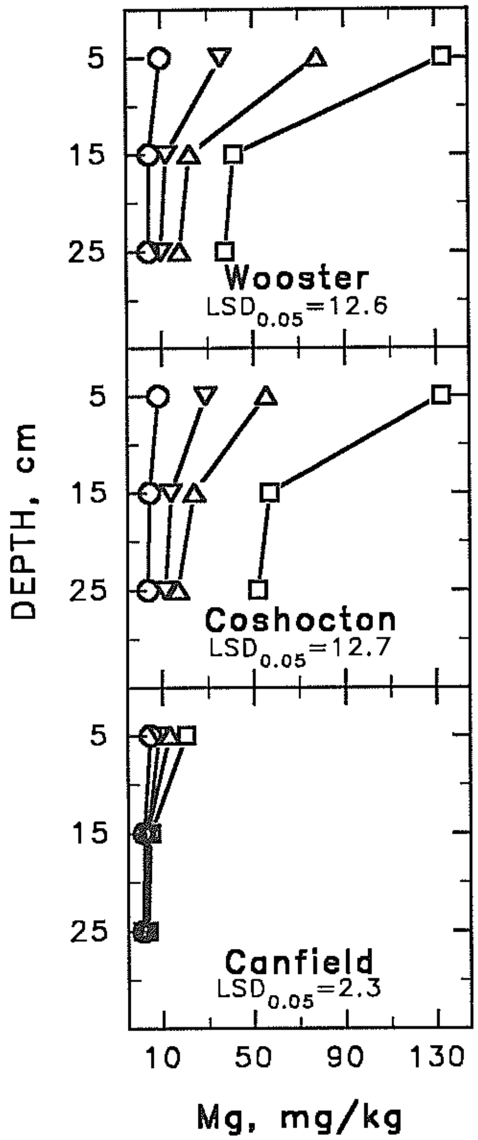

Figure 4. Distribution of water soluble Mg in three soils in the spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ = 1xLR, □ = 2xLR).

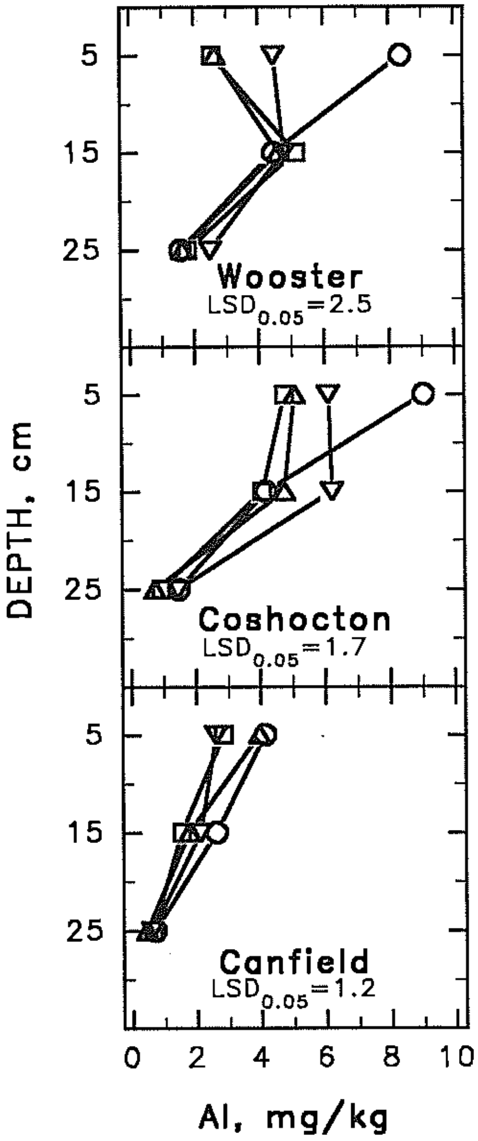

Figure 5. Distribution of water soluble Al in three soils in the spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ = 1xLR, □ = 2xLR).

to PFBC application on any of the three soils (data not shown). Thus there appears to be a very low potential for surface- or ground-water contamination, or increased plant uptake of any of these potentially toxic elements, resulting from application of PFBC at agricultural rates.

Plant Growth

Much of eastern Ohio suffered from a midsummer drought in 1993. No significant precipitation occurred at any of the three sites from July 12 until September 2, with the exception of a 25 mm rain at Canfield on July 29. This drought severely reduced alfalfa and corn growth and yield and overshadowed any PFBC effects.

Corn grain yield was not affected by PFBC in the Wooster or Canfield soils (fig. 9). In the Coshocton

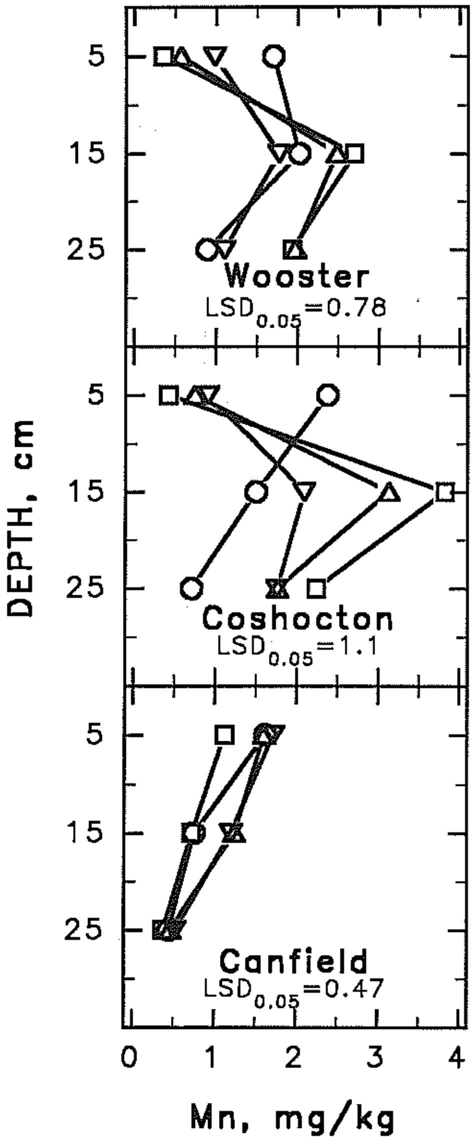

Figure 6. Distribution of water soluble Mn in three soils in the spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ =1xLR, □ = 2xLR).

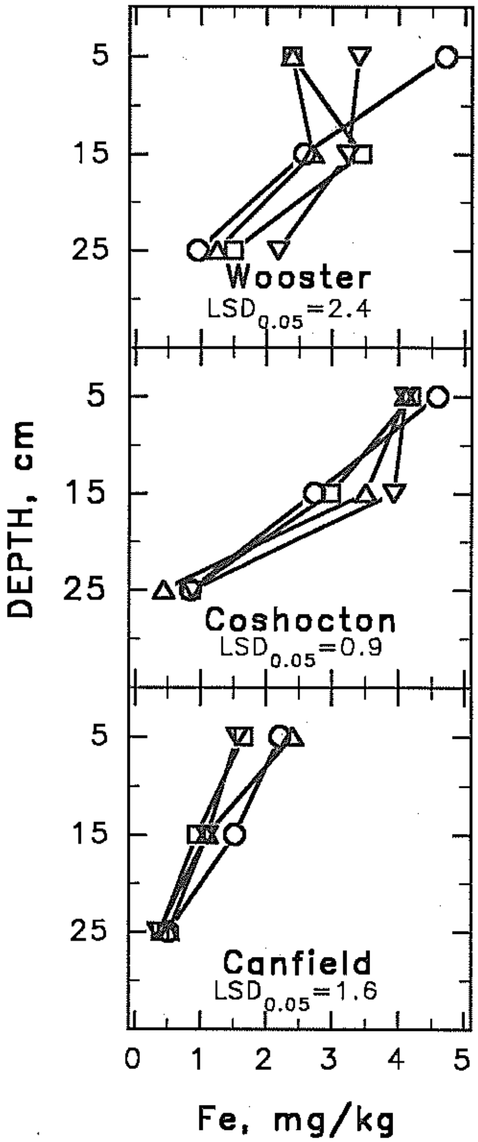

Figure. 7. Distribution of water soluble Fe in three soils in the spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ =1xLR, □ = 2xLR).

soil, PFBC application decreased yield; at the 2xLR rate (45.7 Mg/ha) yield was lower than on the unamended soil. Yield suppression from application of high rates of fluidized bed byproducts has been reported with peanuts (Terman et al. 1979) and red clover (Stout et al. 1979) and has been attributed to high alkalinity and/or high soluble salt content. Given the low soil moisture conditions during the drought period, increased salts in the soil solution may have affected corn growth in our experiment. Good alfalfa growth was obtained only for the first harvest at Wooster, where a large beneficial effect of PFBC application was seen (fig. 9). The second cutting at the Wooster site also showed a positive effect from PFBC application, but yields were severely reduced because of the drought conditions. Poor stand establishment at Coshocton and Canfield, together with drought conditions, resulted in poor yields and no treatment effects on alfalfa yields.

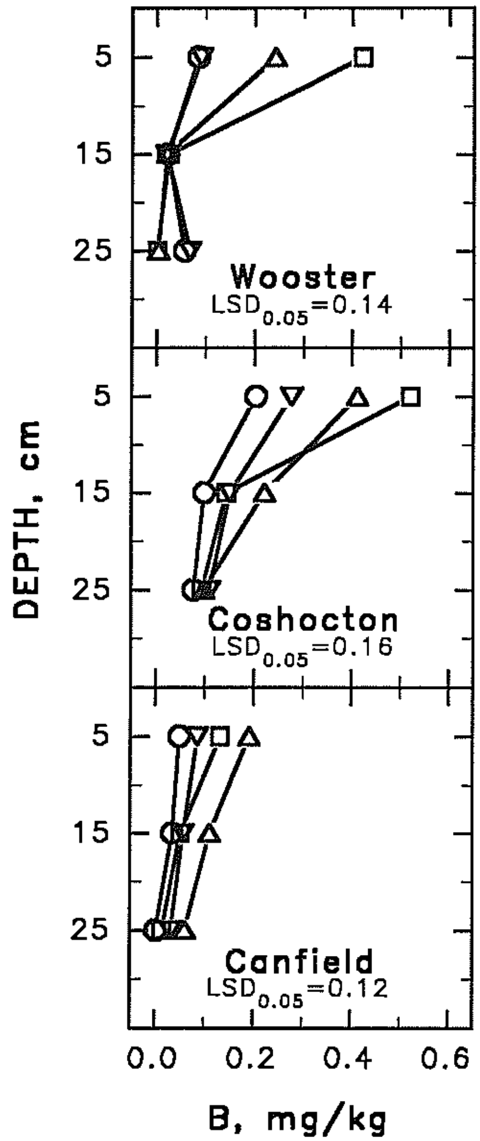

Figure 8. Distribution of water soluble B in three soils in the spring following fall application of PFBC (○ = 0xLR, ▽ = 0.5xLR, △ = 1xLR, □ = 2xLR).

Conclusions

The data presented in this paper represent only one year of data and the following conclusions must, therefore, be considered preliminary. Nevertheless, there is strong evidence that soil application of PFBC at the recommended liming rate effectively neutralized acidity in the zone of incorporation and showed some evidence of increasing pH in underlying soil 6 months after application. Soil chemistry was also made more favorable for plant growth. Water-soluble concentrations of Al, Mn, and Fe were decreased, and the base status of acid soils was improved. The base status of soil below the zone of incorporation was also improved owing to transport of Ca and Mg. Mobility of Ca and Mg in PFBC is greater than in dolomitic limestone because of the greater solubility of $CaSO_4$ and $MgSO_4$ compared with that of $CaMg(CO_3)_2$. There was no evidence that land application of PFBC at the recommended liming rate would lead to elevated levels of potentially toxic trace elements in soil or water.

With pH-sensitive crops such as alfalfa, PFBC application has the potential to improve growth and yield on acid soils. Even when applied at 2xLR there was no adverse effect on yield. With a crop such as corn that is less pH sensitive, the potential yield benefit from PFBC application may be less. While no yield improvement was seen in this study, we believe this was due to drought conditions. In a more normal rainfall growing season we believe there would be greater potential for corn yield to be improved by PFBC application.

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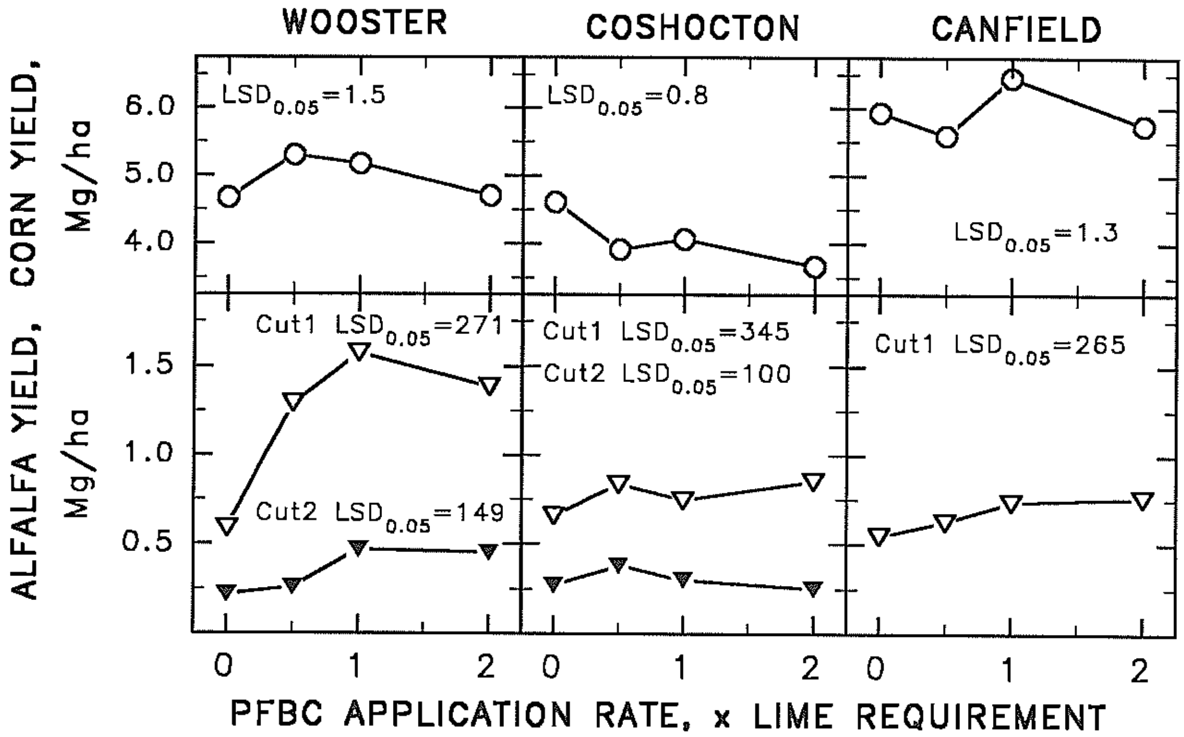

Figure 9. Alfalfa forage yield and corn grain yield on three soils amended with PFBC (o = corn grain yield, ∇ = first cut alfalfa yield, ▼ = second cut alfalfa yield).

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