

**Use of Clean Coal Technology By-Products as Agricultural Liming Techniques**

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## USE OF CLEAN COAL TECHNOLOGY BY-PRODUCTS AS AGRICULTURAL LIMING MATERIALS

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### Abstract

Dry flue gas desulfurization (FGD) by-products are mixtures of coal fly-ash, anhydrite ( $\text{CaSO}_4$ ), and unspent lime- or limestone-based sorbent. Dry FGD by-products frequently have neutralizing values greater than 50%  $\text{CaCO}_3$  equivalency and thus have potential for neutralizing acidic soils. Owing to the presence of soluble salts and various trace elements, however, soil application of dry FGD by-products may have adverse effects on plant growth and soil quality. The use of a dry FGD by-product as a limestone substitute was investigated in a field study on three acidic agricultural soils (pH 4.6, 4.8, and 5.8) in eastern Ohio. The by-product (60%  $\text{CaCO}_3$  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 immediately after FGD application and three more times every six months thereafter. Samples were 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. Within one year pH increases could be detected at depths up 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 all three soils, and had no effect on corn yield. No detrimental effects on soil quality were observed.

### Introduction

The 1990 amendments to the Clean Air Act mandate a two-stage, 10-million ton reduction in annual  $\text{SO}_2$  emissions in the United States by the year 2000. One strategy for meeting this standard is for utilities to scrub  $\text{SO}_2$  from flue gases. Dry flue gas desulfurization (FGD) processes utilize lime-based sorbents in various scrubber vessels and produce highly alkaline by-products which contain unspent sorbent, coal ash, and the  $\text{SO}_2$  reaction product anhydrite ( $\text{CaSO}_4$ ). These by-products 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 by-products would significantly reduce the cost of  $\text{SO}_2$  scrubbing.

Because of their alkalinity, one possible beneficial use for dry FGD by-products is as a

limestone substitute for amendment of acidic agricultural soils. Land application of fluidized bed combustion by-products (one type of dry FGD by-product) as a lime substitute and a source of Ca and S has been investigated in a number of studies<sup>1,2,3,4</sup>. 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, with little emphasis on potential environmental impacts. In this study we have investigated the responses of two crops (alfalfa and corn) grown on three acidic agricultural soils amended with a dry FGD by-product 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 acidic agricultural soils located at Wooster, Coshocton, and Canfield in eastern Ohio. Characteristics of these soils are given in Table 1. Dry FGD by-product was obtained from a pressurized fluidized bed combustion (PFBC) boiler. The PFBC boiler produced two by-product streams: a coarse, granular bed material, and a much finer, particulate material collected in a primary cyclone (Table 2). The PFBC by-product 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<sup>5</sup>. The amount of calcium carbonate required to raise the soil pH to 7 was divided by the CaCO<sub>3</sub> 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 of 1993 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<sup>6</sup> 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 immediately after FGD application and every 6 mo thereafter. Sampling depth ranged from 20 to 60 cm and was done in 10-cm depth increments. 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 through a 0.45- $\mu$ m 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.

In 1993, alfalfa was cut in July and September at the Wooster and Coshocton locations, and in July at the Canfield location, while corn grain was harvested at all three locations in October. In 1994, the first cutting of alfalfa was made in early June at all three locations.

## Results

### *Soil Chemistry*

The PFBC material was clearly effective as a liming material. Soil pH was rapidly raised in the Wooster and Coshocton soils, and the increase was sustained through the spring of 1994 (Fig. 1). In the Canfield soil no effect on pH was seen immediately after incorporation, although pH in the zone of incorporation did increase during the next 8 mo with the 2xLR rate. Apparently the SMP buffer underestimated the lime requirement of this moderately acidic soil, and an insufficient amount of PFBC was applied.

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. The greatest effects on water soluble concentrations of Ca, Mg, and S occurred in the Wooster and Coshocton soils where the 1xLR rates were 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. In the Wooster and Coshocton soils there was very definite movement of surface applied Ca, Mg, and S to a depth of at least 60 cm within the first year after surface application. Such rapid movement was expected with S which was present almost entirely as the sulfate anion ( $\text{SO}_4^{2-}$ ). In the case of Ca and Mg, both of which were present as divalent cations, this represented more rapid movement than would be expected to result from surface application of either limestone ( $\text{CaCO}_3$ ) or dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). The greater mobility of Ca was because much of the Ca in the PFBC was present as  $\text{CaSO}_4$ , which is over 100 times more soluble than  $\text{CaCO}_3$ , and thus more likely to be leached downward. While most of the Mg in PFBC was present in the form of  $\text{MgCO}_3$ , its mobility in soil was greatly increased by the presence of  $\text{SO}_4^{2-}$ . This was because when these two moieties dissolved they formed the relatively stable ion pair  $\text{MgSO}_4^0(\text{aq})$ . This phenomenon was confirmed in a separate study which involved geochemical modeling of leachates from PFBC-amended minespoils<sup>7</sup>. Because of its neutrality, this ion-pair was highly mobile in soil. The rapid movement of Ca and Mg results in a substantial increase in the base-status of sub-soils well below the zone of incorporation and represents a beneficial aspect of FGD by-products not realized with conventional liming materials.

Surface-soil concentrations of water-soluble Al, Fe, and Mn, ions which are frequently phytotoxic in acidic soils, were decreased by PFBC amendment in all three soils (Fig. 3). This can be attributed to the increase in pH that occurred in these soils (Fig. 1), because the solubility of these ions is known to decrease as pH increases above the acid range<sup>8</sup>. 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. In the case of the Wooster soil, and to a lesser extent in the Coshocton and Canfield soils, Al and Fe were decreased throughout the profile even though there was no

change in pH below approximately 30 cm. There is some evidence in the literature that this may be caused by precipitation of Al, and possibly Fe, with  $\text{SO}_4^{2-}$  <sup>9</sup>.

By contrast, Mn in the Wooster and Coshocton soils was increased below the surface soil layer, apparently because of Mn mobilization from the zone of incorporation to the underlying soil. The mobilization of Mn appeared to be the result of cation exchange of  $\text{Mn}^{2+}$  with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Availability of Mn transported deeper in the profile was increased because of the lower soil pH below 10 cm. Thus, while Al and Fe phytotoxicity were decreased throughout the upper 60 cm of these soils, Mn phytotoxicity may have been increased deeper in the profile. It should be noted, however, that there was no evidence of Mn toxicity in alfalfa or corn grown on any of the FGD-amended plots.

Of the trace elements, only B was affected by PFBC amendment (Fig. 4). Concentrations of water-soluble B were increased in the zone of PFBC incorporation in all three soils. The coal fly ash component of the PFBC material is the primary source for the B and elevated B, or B phytotoxicity, has been reported in several studies involving land application of coal fly ash<sup>10</sup>. 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 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. 5). In the Coshocton 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 by-products has been reported with peanuts<sup>4</sup> and red clover<sup>3</sup> 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.

In 1993, good alfalfa growth was obtained only for the first harvest at Wooster, where a large beneficial effect of PFBC application was seen (Fig. 5). 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. In the second growing season, 1994, alfalfa stands were well-established and yield response to FGD amendment was seen at all three locations (Fig. 6). Plant tissue analyses showed FGD amendment increased B, Mg, Mo and S in alfalfa grown at Wooster and Coshocton (data not shown). Tissue concentrations, however, remained within sufficiency ranges for these elements.

## Conclusions

Soil application of PFBC at the recommended liming rate effectively, and rapidly neutralized acidity in the zone of incorporation, and showed evidence of increasing pH in underlying soil to a depth of 30 cm within one year of application. Soil chemistry was also made more favorable for plant growth. The increased pH in the zone of incorporation resulted in an immediate decrease in water-soluble concentrations of Al, Fe, and Mn, while Ca, Mg, and S were increased. Owing to the greater solubility of  $\text{CaSO}_4$  and  $\text{MgSO}_4$  compared to that of  $\text{CaMg}(\text{CO}_3)_2$ , Ca, Mg, and S were rapidly transported through the soil profile and resulted in increased base status and decreased Al and Fe well below the zone of incorporation. Mobilization of Mn from the zone of incorporation to lower pH subsoil resulted in increased Mn concentrations in the subsoil. 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 increased growth and yield on acidic 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.

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

Soil	Classification	LR <sup>1</sup> , Mg/ha	pH	Bray P <sub>1</sub> , mg/kg	Exchangeable, mg/kg			CEC <sup>2</sup> , cmol <sub>c</sub> /kg
					K	Ca	Mg	
Wooster	Aquic Fragiudalf	20.6	4.6	9	103	430	85	15.7
Coshocton	Aquatic Hapludalf	13.7	4.8	9	118	300	87	12.1
Canfield	Typic Fragiudalf	2.8	5.8	29	171	1130	29	8.7

<sup>1</sup> Lime requirement, amount of ag-lime required to raise soil pH to 7.

<sup>2</sup> Cation exchange capacity.

Table 2. Characterization of PFBC by-products.

Parameter		PFBC, cyclone	PFBC, bed
pH		10.5	12.2
CCE, %		60.3	60.0
Particle size distribution, %			
>2 mm		0.0	4
2-0.1 mm		0.0	95
100-50 $\mu$ m		23.5	1
50-2 $\mu$ m		76.1	0
<2 $\mu$ m		0.4	0
Major minerals, %			
Dolomite		25	ND <sup>1</sup>
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

<sup>1</sup>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 <sup>1</sup>	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

<sup>1</sup>Lime requirement, amount of ag lime required to raise soil pH to 7.

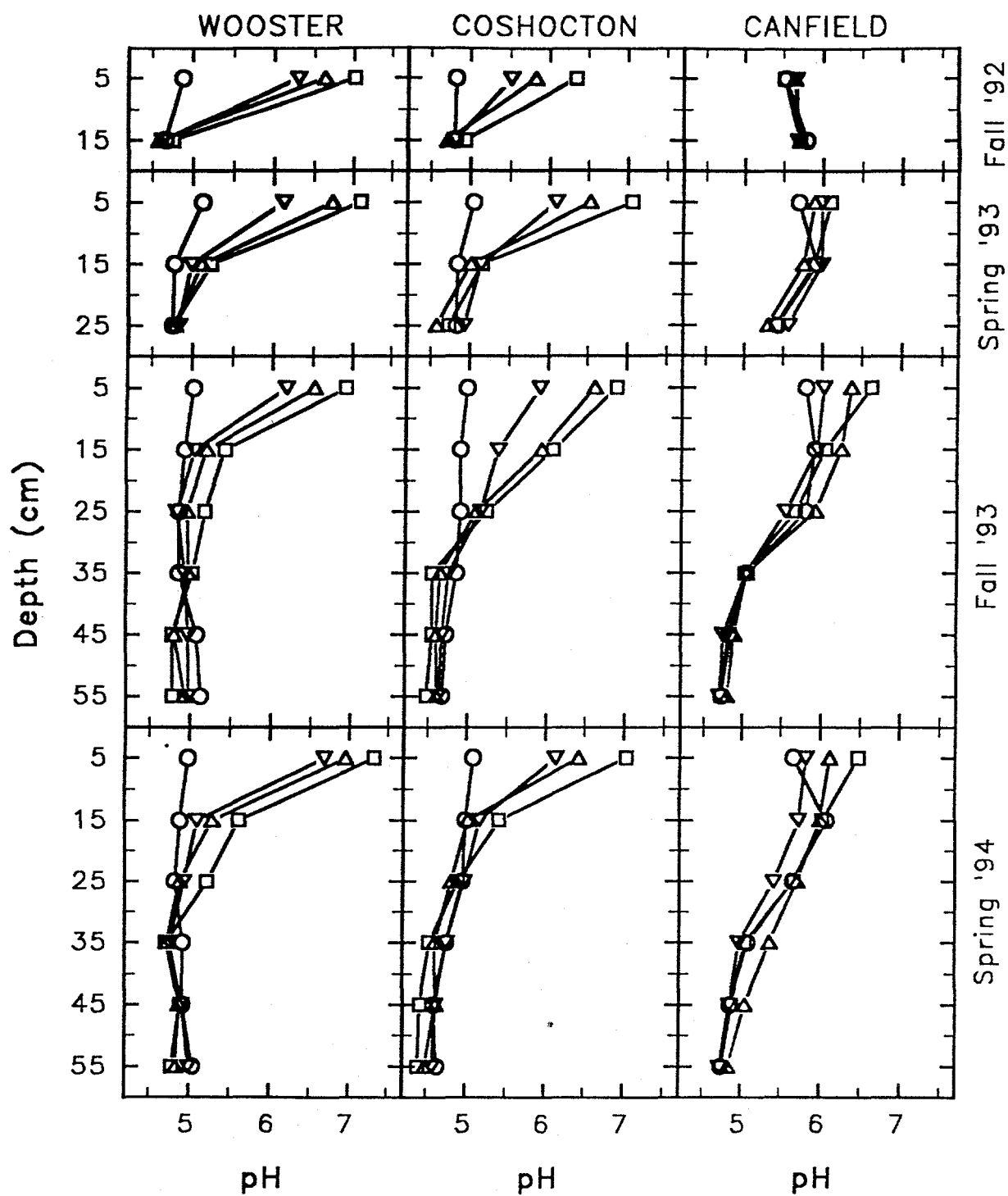


Figure 1. Distribution of pH in Wooster, Coshocton, and Canfield soils following fall 1992 application of PFBC by-product ( $\circ$ =0xLR,  $\nabla$ =0.5xLR,  $\Delta$ =1xLR,  $\square$ =2xLR).

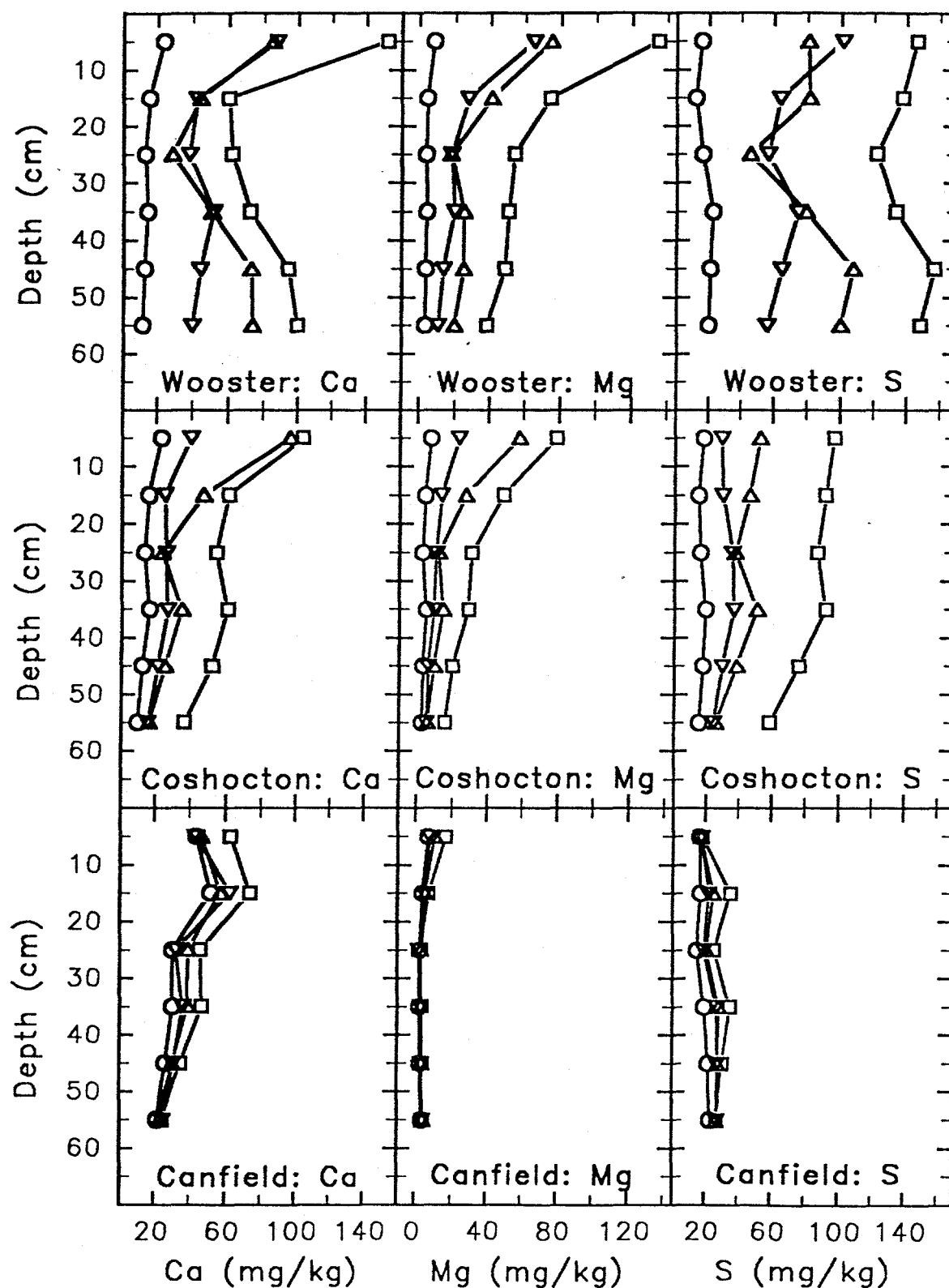


Figure 2. Distribution of Ca, Mg, and S in Wooster, Coshocton, and Canfield soils one year after fall 1992 application of PFBC ( $\circ$ =0xLR,  $\nabla$ =0.5xLR,  $\Delta$ =1xLR,  $\square$ =2xLR).

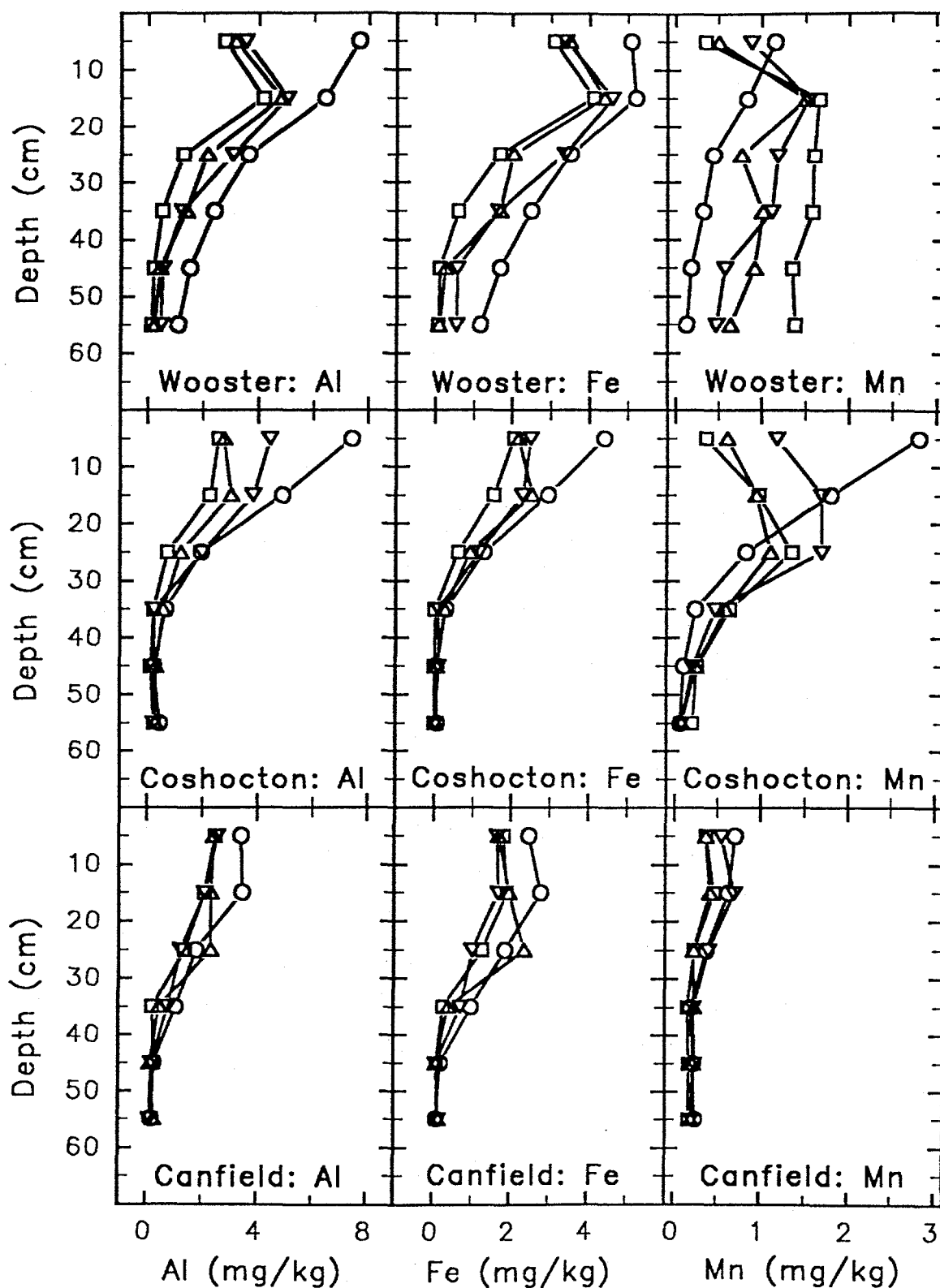


Figure 3. Distribution of Al, Fe, and Mn in Wooster, Coshocton, and Canfield soils one year after fall 1992 application of PFBC ( $\circ$ =0xLR,  $\nabla$ =0.5xLR,  $\Delta$ =1xLR,  $\square$ =2xLR).

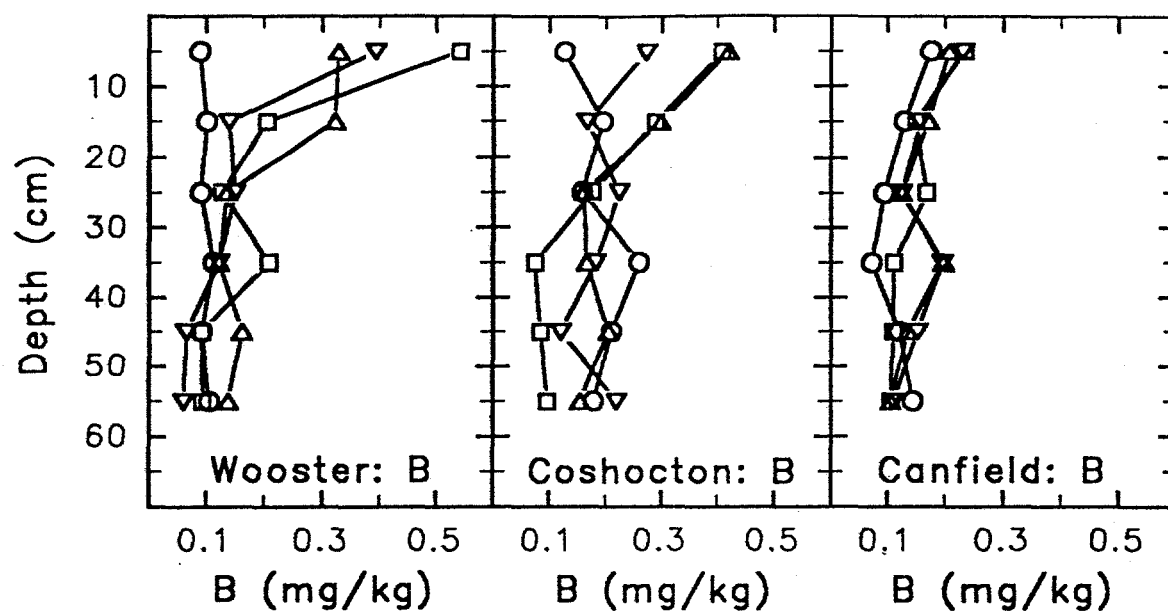


Figure 4. Distribution of B in Wooster, Coshocton, and Canfield soils one year after fall 1992 application of PFBC by-product ( $\circ$ =0xLR,  $\nabla$ =0.5xLR,  $\Delta$ =1xLR,  $\square$ =2xLR).



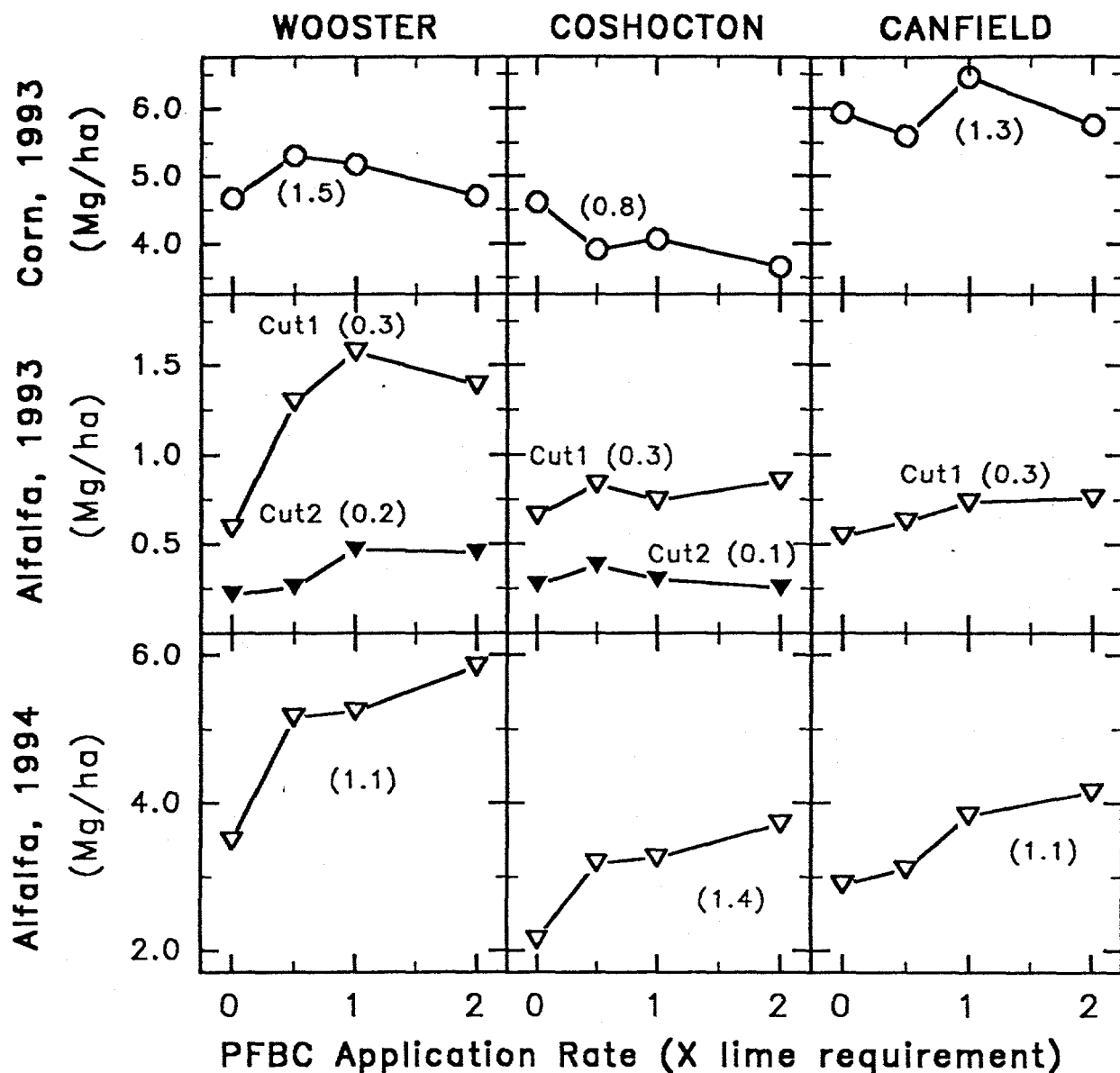


Figure 5. Corn and alfalfa yield on Wooster, Coshocton, and Canfield soils following fall 1992 application of PFBC by-product.