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Effect of Coal Combustion By-products on Phosphorus Runoff from a Coastal Plain Soil

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Coal combustion by-products can lower soil phosphorus (P) solubility, but few studies have assessed their effect on runoff P. A soil with elevated P content was amended with fluidized bed combustion ash, flue gas desulfurization gypsum, and anthracite refuse ash at rates of 0–40 g kg⁻¹ soil, and runoff from small plots was monitored over 3 years. In the first year, by-products lowered dissolved P in runoff by up to 47% below the untreated control; however, effects did not persist into the remaining years of the study. Total P losses were not significantly affected by coal combustion by-products, likely because of elevated particulate P losses. Water-extractable P was up to 40% less in treated soils than in untreated soils across the 3 years. Results demonstrate that although coal combustion by-products readily lower P solubility in soils, their impact on P losses in runoff can be undermined by erosional processes.

Keywords Fly ash, phosphorus, water quality

Introduction

Effects of phosphorus (P) runoff from agricultural soils on water quality is a widespread concern because of the role of P in accelerating the eutrophication of freshwater systems (Carpenter et al. 1998). Long-term application of manure to agricultural soils can enrich P pools that are readily available to runoff (Graetz and Nair 1995; Ebeling et al. 2002). Many studies document strong correlations between soil-test P and dissolved P concentrations in runoff (Pote et al. 1999). On the Delmarva Peninsula (Delaware, Maryland, and Virginia), particularly in areas of intensive poultry production, losses of P in runoff are of concern

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This paper is dedicated to the memory of William (Bill) Stout, mentor, friend, and passionate conservationist.

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given the mounting soil P levels and the immediate proximity to the Chesapeake Bay (Sims and Kleinman 2005). This important estuary and its tributaries are prone to both nitrogen (N)- and P-induced eutrophication (Boesch, Brinsfield, and Magnien 2001).

Although many best-management practices are used to control P in runoff from agricultural soils, most are geared toward controlling particulate P transfers arising from soil erosion (Sims and Kleinman 2005). Few options exist to lower dissolved P losses in runoff from soils that are already high in P (Sharpley 2003). One area of growing interest has been the use of amendments that decrease P availability to runoff water (Novak and Watts 2005). A variety of studies show that treating poultry litter with alum can decrease water-extractable P (WEP) in litter. When litter is then applied to land, dissolved P losses in runoff are lowered (Moore, Daniel, and Edwards 2000; Smith et al. 2004). Other amendments that have been evaluated in early laboratory studies are P-sorbing materials. For instance, Codling, Chaney, and Mulichi (2000) observed reductions in WEP after incubating soils and poultry litter in pots with municipal by-products. Similarly, Peters and Basta (1996) observed reductions in WEP from soils amended with aluminum (Al)-enriched solids from water treatment plants and iron (Fe)-enriched bauxite mixed with calcium (Ca)-enriched gypsum. Although such studies effectively demonstrate the potential to lower P solubility in soils, they do not directly measure P loss in runoff and thus provide limited information on other factors that help determine their suitability as an agricultural amendment. To be an appropriate agricultural amendment, a P-sorbing material should be nondeleterious to crop production and possess favorable agronomic qualities. Most important, an amendment must not create hazards with regard to soil, water, and crops and should be economically feasible.

One source of materials that has been considered for use in agriculture is the electric industry's coal combustion by-products (CCPs). A total of approximately 2 million tons of coal ash (fly and bottom ash) is generated annually from Maryland plants (Maryland Department of the Environment 2009). The most abundant CCP is coal ash (Punshon, Adriano, and Weber 2001), a mix of amorphous, ferro-alumino silicate minerals (Ghodrati, Sims, and Vasilas 1995; Adriano et al. 1980), along with a diverse array of constituents that include arsenic (As), boron (B), Ca, molybdenum (Mo), sulfur (S), and selenium (Se) (Page et al. 1979; Kost, Elseewi, and Straughan 2005). In addition to coal ash, CCPs include materials from the flue gas desulfurization (FGD) process where lime is used to remove S from gaseous emissions during combustion of high S coal (Punshon, Adriano, and Weber 2001). These materials are alkaline and contain calcite, dolomite, calcium oxide, calcium hydroxide, gypsum, calcium sulfite, magnesium sulfate, magnesium oxide, and fly ash (Crews and Dick 1998). Generally, FGD by-products do not possess an abundance of trace elements (Punshon, Adriano, and Weber 2001).

Considerable precedent exists for using CCPs as soil amendments in agriculture. For example, studies have shown the potential for using CCPs amendments on agricultural soils to lower subsoil acidity (O'Reilly and Sims 1995; Sims, Vasilas, and Ghodrati 1995), improve soil texture and water-holding capacity by increasing aeration (Sell et al. 1989), improve soil infiltration properties (Kukier, Sumner, and Miller 2001), reduce bulk density (Chang et al. 1977), enhance soil fertility (Carlson and Adriano 1993), and improve crop yields (Stout and Priddy 1996). Simultaneously, concerns over the use of CCPs in agriculture have also been raised. Studies have shown that CCPs can potentially cause phytotoxicity from soluble elements, especially trace elements that adversely affect crop, soil, and possibly water quality (Adriano et al 1980; Sims, Vasilas, and Ghodrati 1995; Matsi and Keramidis 2001). Careful selection of CCPs and application at appropriate rates are therefore required if these materials are to be recommended for use in agriculture (Korcak 1995).

Others have also evaluated the use of CCPs as a potential P-sorbing material to remediate high-P soils in laboratory studies. For instance, Stout, Sharpley, and Pionke (1998) reported fluidized bed coal ash (FBC) and FGD by-product incubation (10 g kg^{-1}) with soil reduced WEP by 60% and 50% respectively. Elsewhere, Callahan *et al.* (2002) found that incubation with FBC and FGD (40 g kg^{-1}) reduced WEP by at least 50%. In one of the few field studies evaluating CCPs as P-sorbing amendments, Stout, Sharpley, and Landa (2000) reported that FBC and FGD reduced dissolved P in runoff by 20% and 43%, respectively, when incorporated in the surface 5 cm of an acidic ($\text{pH} = 6.0$) soil at 20 g kg^{-1} .

The mechanisms by which CCPs decrease P solubility are not fully understood given their heterogeneous nature and interaction with soil particles. In the case of FBC, high concentrations of Ca are thought to promote the formation of Ca phosphates, which are stable in neutral and alkaline soils but less so in acidic soils (Lindsay 1979). As a result of being a comparatively good liming agent (Callahan *et al.* 2002), application of FBC to moderately acidic soil can increase soil pH sufficiently to cause possible formation of Ca phosphates. When FBC is used in acidic soils, applied Ca likely displaces exchangeable Fe and Al via mass action (Brady and Weil 1996), increasing Fe and Al in the soil solution and promoting the formation of Fe and Al phosphates, which are relatively stable in acidic soils (Lindsay 1979). This mechanism has also been hypothesized for increased P sorption in FGD-amended soils (Stout, Sharpley, and Landa 2000). For anthracite refuse ash (ARA), mechanisms of P sorption are by both Fe and Al, either in the form of electrolytes or hydrous minerals (Callahan *et al.* 2002).

This study evaluated the potential for using CCPs in conventional corn production on an acidic soil with Mehlich 3 P concentrations well in excess of crop requirements (338 mg kg^{-1}). Specific objectives of this study were to determine the effectiveness of CCPs in reducing P losses in runoff as a function of CCP type, application rate, and time as well as to assess the effect of CCPs on soil properties tied to P cycling.

Materials and Methods

Study Site

This study was conducted on a 2-ha field within the University of Maryland Eastern Shore (UMES) research farm ($38^\circ 12' 22'' \text{ N}$ and $75^\circ 40' 35'' \text{ W}$) in Princess Anne, Maryland. The farm, formerly a commercial poultry operation with a 30-year history of intensive poultry litter application, was purchased by UMES in 1996. Soils grade from the poorly drained Othello series (fine-silty, mixed, active, mesic Typic Endoaquult) to the well-drained Matapeake series (fine-silty, mixed, semi-active, mesic Typic Hapludult). Soils have an average slope of 3% and high concentrations of P (Mehlich 3 P $> 300 \text{ mg kg}^{-1}$) due to a long history of receiving poultry litter at rates often exceeding annual crop removal (Kleinman *et al.* 2007). Soils were cropped in corn–wheat–soybean rotation. Temperature and precipitation measurements, recorded on a continual (5-min) basis over the 3-year study period, were 115 cm yr^{-1} (excluding snowfall) and 13° C (monthly averages ranged from 4° C to 25° C).

Surface Runoff Experiment

Forty-eight surface runoff plots ($60 \times 120 \text{ cm}$) were established within the UMES research farm by a modified design of Stout, Sharpley, and Landa (2000). Runoff plots consisted of painted steel borders (15 cm high) pushed 10 cm into the soil with a covered gutter located

Table 1
Select properties of coal combustion byproducts used
in runoff study

Property	Coal combustion byproduct		
	ARA	FBC	FGD
Relative P sorption potential			
P sorbed (mg kg ⁻¹)	999	998	109
Solution P (mg L ⁻¹)	0.24	1.67	890
pH (1:1 water)	10.7	12.8	7.8
Solids (%)	97.5	99.2	82
2 M KCl extractable [†]			
Al (mg kg ⁻¹)	nd [‡]	nd	nd
Ca (mg kg ⁻¹)	1108	2728	2189
Fe (mg kg ⁻¹)	nd	nd	nd
P (mg kg ⁻¹)	nd	nd	nd
S (mg kg ⁻¹)	853	1766	1863
Elemental content, % of total			
Al	3.5	2.1	0.01
Ca	3.6	14.8	6.2
Fe	1.3	2.2	0.03
P	0.02	0.04	0.02
S	0.89	2.5	5.1

[†]KCl = extractable and total elemental concentrations are on a dry weight basis

[‡]nd = non-detectable (concentration in extract below detection limit of ICP-AES)

at the lower front end of each plot. An 8-L collection bottle was housed inside of a buried 20-L bucket (with top lid) to collect runoff.

Three by-products (ARA, FBC, FGD) obtained from power plants in Pennsylvania (Table 1) were applied to plots in a randomized complete block design with four replications. Generally, but not in all cases, these materials contain high-quality gypsum (CaSO₄) and low levels of trace elements. Coal combustion by-products were applied at four rates (0, 10 20, and 40 g CCP kg⁻¹ soil) and incorporated into the upper 5 cm of soil in March 2000 (the first year of study only). Rates were selected to give a range of expected WEP concentrations in the amended soils based upon a laboratory study of Stout, Sharpley, and Landa (2000).

Runoff and Soil Sampling. Runoff was monitored on a storm-event basis from March 2000 to September 2002. When runoff was present, the total volume was recorded and a 250-mL subsample was retained in a plastic bottle that was stored at 4 °C within 1 h of collection. Samples were collected, filtered (0.45- μ m filter), and analyzed immediately, in some cases within 1 week of filtering. The first rain event occurred within 2 to 3 weeks after CCPs were applied.

Six soil cores (2-cm diameter) were obtained from the upper 15 cm within each runoff field plot on three occasions during the study: October 2000 (7 months after

CCP application); April 2002 (25 months after CCP application); and September 2002 (30 months after CCP application). All cores from a single plot were thoroughly mixed, and a 50-g composite sample was obtained for analysis. Soil was air dried (25 °C) and sieved (2-mm) prior to laboratory analysis.

Laboratory Analysis

Coal Combustion By-products. All CCP samples were run in triplicate. Readily desorbable Al, Ca, Fe, and P were determined by shaking CCPs with 2 M potassium chloride (KCl) (solid/solution = 1:5) for 30 min. Following filtration (Whatman No. 1), the supernatant was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Total elemental analysis of CCPs was determined by EPA method 3050/3051 (U.S. Environmental Protection Agency 1986), with digests analyzed by ICP-AES for Al, Ca, Fe, P, and S. Single-point sorption experiments were conducted to evaluate the relative P-sorption potential of CCPs prior to their addition to soil. A solution containing 1000 mg P L⁻¹ [as monopotassium phosphate (KH₂PO₄) in 0.01 M calcium chloride (CaCl₂)] was shaken with each of the CCPs for 24 h (solid/solution = 1:25). The mixture was filtered (Whatman No. 1) and the supernatant analyzed for P by modified colorimetric method of Murphy and Riley (1962), at a wavelength of 712 nm. The amount of P sorbed (mg P kg⁻¹) and equilibrium solution concentration (mg L⁻¹) were used as indicators of relative P-sorption potential. The pH of CCPs was determined in a water (solid/solution = 1:1).

Runoff Water. Dissolved P was determined on filtered (0.45- μ m) water samples by colorimetry. Total P was determined on unfiltered samples by a semi-micro-Kjeldahl digestion procedure (Bremner 1996), with P in digests determined by colorimetry. Total solids were determined by gravimetric analysis, after evaporating 200 mL of unfiltered runoff water at 80 °C.

Soils. Soil samples were analyzed for Mehlich 3-extractable P, K, Ca, and Mg by shaking soil and Mehlich 3 solution [0.2 N acetic acid (CH₃COOH), 0.25 N ammonium nitrate (NH₄NO₃), 0.015 N ammonium fluoride (NH₄F), 0.013 N nitric acid (HNO₃), and 0.001 N ethylenediaminetetraacetic acid (EDTA)] for 5 min (soil/solution = 1:10), followed by filtration (Whatman No. 1) and analysis of the supernatant by ICP-AES (Mehlich 1984). Water-extractable soil P was measured by shaking soil and deionized water (soil/solution = 1:10) for 1 h, followed by filtration (Whatman 1) and colorimetric determination of P (Murphy and Riley 1962). Soil pH was determined in distilled water (soil/solution = 1:1).

Statistical Analysis

Statistical analyses were conducted using SAS, version 8 (SAS Institute Inc. 1999). Data were analyzed by SAS's PROC Univariate to confirm assumption of normality and equal variance distribution. Runoff P and sediment data were analyzed on an annual basis, with concentration data (mg L⁻¹) for individual runoff events weighted relative to total annual flow volumes. All data were analyzed by the general linear model, using Duncan's test for pairwise comparison of means. Differences discussed in the text were significant at $\alpha \leq 0.05$.

Results and Discussion

Properties of Coal Combustion By-products

The CCPs (FGD, FBC, and ARA) used in this study exhibited key differences with respect to properties salient to soil P chemistry (Table 1). Single-point sorption experiments revealed substantial differences in relative P sorption potential of the CCPs prior to their application to soil. Both ARA and FBC sorbed nearly all of the P from solution, while FGD sorbed relatively little. Equilibrium solution P concentrations followed the trend of $FGD \gg FBC > ARA$, implying that FGD is considerably less effective at maintaining low solution-P concentrations than either FBC or ARA. It is important to reiterate that these sorption properties point to inherent differences in CCPs prior to their addition to soil. Once applied to soils, interactions between CCPs and soil will likely modify their relative sorption potentials. Thus, it appears as though these types of sorption studies are probably not good indicators of the potential impact of effects of CCPs treatments on P in surface runoff.

Callahan et al. (2002) found FGD to be more effective in promoting P sorption than ARA when mixed with acidic soils. All CCPs had low concentrations of total P and non-detectable concentrations of 2 M KCl extractable P, suggesting that their addition to soil should not substantially increase either total or readily desorbable P. Relative differences in pH of the three CCPs used (Table 1) were similar to differences in CaCO₃ equivalency values reported by Callahan et al. (2002), for FBC (CaCO₃ equivalent = 57%), ARA (CaCO₃ equivalent = 21%), and FGD (CaCO₃ equivalent = 16%).

The CCPs used in this study contained varying amounts of Ca, Fe, and Al, with Al being the smallest for FGD (Table 1), all of which are known to decrease the solubility of P under certain environmental conditions. Fluidized bed combustion coal ash (pH = 12.8) contained a large concentration of total Ca (14.8%) but a relatively small concentration of 2 M KCl-extractable Ca (0.3%). Compared with Ca, lesser concentrations of total Fe and Al were found in FBC, and neither Fe nor Al was detectable in 2 M KCl extracts (Table 1). Elsewhere, Callahan et al. (2002) reported that Ca compounds serve as the primary control on P solubility in FBC. Anthracite refuse ash (pH = 10.7) contained a lesser concentration of total Ca (3.6%), with approximately 0.1% extractable by 2 M KCl. As with FBC, total Fe and Al were found in lesser concentrations, with none detectable in 2 M KCl extracts. These findings appear to contrast with those of Callahan et al. (2002), who identified Fe as the dominant control of P solubility in ARA and suggest instead that Ca may serve as a key control of P solubility when ARA is applied to soil. Analysis of FGD, which is purported in most cases, but not all, to consist primarily of gypsum, revealed a low concentration of total Ca (6.2%) and total S (5.1%) content, with 2 M KCl-extractable Ca and S concentrations near 0.2%. These findings suggest a relatively low gypsum content in the FGD used in the current study, confirming the finding of Kost et al. (2005) that FGD represents a heterogeneous class of materials.

Effect of Coal Combustion By-products on P in Runoff and Soil

Runoff. Rainfall during the study period (2000–2002) was 15–56% less than the long-term average (Table 2). Even so, a total of 32 runoff events were sampled over the course of the study, yielded 14, 11, and 7 events, respectively, in 2000, 2001, and 2002. Concentrations of P in runoff from the unamended control treatments were high (dissolved P averaged .93–2.86 mg L⁻¹, total P averaged 2.97–6.91 mg L⁻¹), as were related losses (dissolved P averaged 2.71–11.14 kg ha⁻¹; total P averaged 11.97–17.66 kg ha⁻¹).

Table 2
Mean annual runoff properties from field plots treated with coal combustion byproducts

CCP treatment	CCP application rate	N	Runoff depth	Runoff P concentration		Runoff P loss	
				Dissolved	Total	Dissolved	Total
				mg L ⁻¹		kg ha ⁻¹	
g kg ⁻¹ cm							
2000 (total rainfall = 98 cm)							
Unamended control	0	12	0.43 a [†]	1.13 a	4.86 a	3.49 a	15.81 a
ARA amended	10	4	0.45 a	0.94 ab	4.37 a	2.99 ab	14.00 a
	20	4	0.44 a	0.65 bc	4.34 a	2.05 bc	13.97 a
	40	4	0.4 a	0.64 bc	4.45 a	1.88 c	13.07 a
FBC amended	10	4	0.41 a	0.74 b	4.52 a	2.09 bc	13.18 a
	20	4	0.44 a	0.63 bc	4.73 a	1.99 bc	15.32 a
	40	4	0.43 a	0.39 c	3.99 a	1.19 c	12.45 a
FGD amended	10	4	0.42 a	0.70 bc	4.11 a	2.13 bc	12.82 a
	20	4	0.46 a	0.63 bc	4.99 a	2.07 bc	16.61 a
	40	4	0.29 b	0.59 bc	3.44 a	1.54 c	8.12 a
2001 (total rainfall = 51 cm)							
Unamended control	0	12	0.39 a	0.93 abc	6.91 a	2.71 ab	17.66 a
ARA amended	10	4	0.38 a	0.95 abc	5.63 a	2.65 ab	15.15 a
	20	4	0.32 a	0.56 bc	6.60 a	1.27 b	15.57 a
	40	4	0.31 a	0.49 b	8.16 a	1.10 b	17.69 a
FBC amended	10	4	0.37 a	1.10 a	7.66 a	3.25 a	20.19 a
	20	4	0.34 a	0.64 abc	5.29 a	1.56 ab	12.67 a
	40	4	0.40 a	0.52 bc	6.21 a	1.53 ab	17.63 a
FGD amended	10	4	0.33 a	0.75 abc	6.62 a	1.81 ab	14.63 a
	20	4	0.37 a	0.99 ab	6.14 a	2.77 ab	16.67 a
	40	4	0.40 a	0.87 abc	6.61 a	2.51 ab	18.22 a
2002 (total rainfall = 70 cm)							
Unamended control	0	12	0.55 ab	2.86 a	2.97 a	11.14 a	11.97 a
ARA amended	10	4	0.53 bc	2.61 a	3.40 a	10.12 a	12.89 a
	20	4	0.56 a	2.25 a	2.91 a	9.09 a	11.77 a
	40	4	0.50 bc	1.95 a	2.91 a	6.82 a	10.78 a
FBC amended	10	4	0.51 bc	2.74 a	3.00 a	10.05 a	11.03 a
	20	4	0.51 bc	2.35 a	2.65 a	8.67 a	9.76 a
	40	4	0.56 a	2.02 a	3.38 a	8.06 a	13.53 a
FGD amended	10	4	0.53 abc	2.49 a	3.24 a	8.98 a	12.15 a
	20	4	0.46 bc	2.71 a	2.37 a	8.69 a	7.55 a
	40	4	0.45 c	2.65 a	2.35 a	8.47 a	7.98 a

[†]Letters represent Duncan's mean groupings ($\alpha = 0.05$) of different runoff properties for CCP and the control treatments, and are meant for comparisons within a single year only (2000, 2001 or 2002).

The effects of CCPs on P in runoff were mixed, with significant declines in dissolved P observed during the first year of the study but not in total P (Table 2). All CCPs were effective in reducing dissolved P concentrations (mg L^{-1}) in runoff in 2000, with maximum declines ranging from 32–55% of dissolved P in runoff from the control plots. These proportional declines in runoff dissolved P are comparable to those observed by Stout, Sharpley, and Landa (2000) for FBC and FGD applied to grassed soils in the Ridge and Valley regions of Pennsylvania. In the current study, differences in runoff dissolved P concentrations in 2000 were clearly affected by CCP application rate. For instance, dissolved P concentrations in runoff were lowest from plots amended with FBC at 40 g kg^{-1} , whereas dissolved P in runoff from plots receiving ARA at 10 g kg^{-1} did not differ significantly from the control. In terms of efficacy, both FBC and FGD achieved significant reductions in runoff P concentrations when applied at only 10 g kg^{-1} . Trends in dissolved P losses (kg ha^{-1}) were generally comparable to those observed in dissolved P concentrations, as flow was similar from most plots. In 2000, flow from only one treatment (FGD applied at 40 g kg^{-1}) differed significantly from the control. The decreased runoff from this treatment, compounded with lower dissolved P concentration, resulted in a dissolved P loss that was only 44% of the control (Table 2).

The influence of CCPs on runoff dissolved P was short-lived, and significant differences were observed only in years 1 and 2. More important, no significant differences in runoff total P were observed between treatments for any of the 3 years of the study (Table 2). It is likely that particulate P, not dissolved P, was the dominant form of P in runoff. For instance, in 2000, dissolved P averaged only 9% to 23% of total P. Although particulate P in runoff was not directly measured, the difference between dissolved P and total P in runoff should primarily reflect particulate sources of runoff P. Thus, from 73% to 91% of total P in runoff was potentially associated with eroded sediments in 2000. The importance of particulate P to total P in runoff is supported by runoff total solids data. Estimated erosion rates averaged 1.20 and 0.98 Mg ha^{-1} in 2001 and 2002, respectively. However, there were no significant differences in erosion. Although the total solid content of runoff was not measured in 2000, there is reason to believe that erosion would have been greater in 2000 than in 2001 and 2002 as soils were freshly cultivated in 2000 to incorporate CCPs. Indeed, total P in runoff was greatest in 2000, consistent with greater erosion that year (Table 2). Undoubtedly, eroded solids included the applied CCPs as well as soil. Thus, erosion may have depleted CCPs from the soil surface, shortening the period during which they affected dissolved P in runoff. It is important to note that the rates of erosion observed in the current study, although substantial, were not uncharacteristic for coastal plain soils in the region. Elsewhere, Inamdar et al. (2001) reported annual erosion rates of only 0.9 – 1.1 Mg ha^{-1} from a row-cropped watershed on the coastal plain of Virginia.

Soil. Trends in soil properties point to a more persistent influence of CCPs on soil P solubility than was observed in runoff. Addition of CCPs to soil significantly decreased WEP of the upper 15 cm of soil relative to the unamended control (Table 3). Averaged across the 3 years of study, mean soil WEP followed the trend of the control (18.4 mg kg^{-1}) > ARA (17.2 mg kg^{-1}) = FBC (16.3 mg kg^{-1}) > FGD (13.4 mg kg^{-1}).

As with runoff, the effects of CCPs on WEP were transient, but in the case of FGD and FBC, the effects persisted longer than the 1-year time frame observed in the runoff study at the greater rates of application (Table 3). Specifically, incorporation of FGD significantly lowered soil WEP in October 2000, 7 months after application. Differences in soil WEP between FGD treatments and the control persisted into 2002, but diminished with time. No significant difference in soil WEP was observed between the control and FGD applied at

Table 3
Select properties of runoff plot soils over the three year evaluation period

Soil property and sampling date	Months after CCP application	Control (unamended)			ARA application rate (g kg ⁻¹)			FBC application rate (g kg ⁻¹)			FGD application rate (g kg ⁻¹)		
		10	20	40	10	20	40	10	20	40	10	20	40
WEP (mg kg⁻¹)													
Fall, 2000	7	20.1 ab [†]	20.3 ab	20 bc	20.3 bc	16.2 bc	13.1 cd	15.3 c	10.1 d	9.5 d			
Spring, 2002	24	15.4 abc	13.9 cd	15.3 bc	17.4 a	16.3 ab	14.9 bcd	15.4 abc	12.9 d	9.1 e			
Fall, 2002	29	19.6 a	16.2 ab	15.3 bc	18.0 ab	16.5 ab	14.4 bc	19.8 a	16.6 ab	11.6 c			
Mehlich-3 P (mg kg⁻¹)													
Fall, 2000	7	369 ab	375 ab	361 ab	372 ab	357 ab	322 c	383 a	361 ab	350 b			
Spring, 2002	24	352 ab	361 a	348 ab	351 ab	345 ab	325 b	356 ab	364 a	339 ab			
Fall, 2002	29	348 ab	349 ab	341 ab	341 ab	326 ab	309 b	365 a	368 a	334 ab			
pH													
Fall, 2000	7	5.2 ef	5.4 ed	5.6 cd	5.8 bc	6.0 b	6.5 a	5.0 fgh	4.9 gh	4.9 h			
Spring, 2002	24	5.3 d	5.3 d	5.8 c	6.1 bc	6.3 b	6.7 a	5.4 d	5.3 d	5.2 d			
Fall, 2002	29	5.0 cd	5.1 cd	5.2 c	5.1 cd	5.9 b	6.8 a	4.9 cd	4.9 cd	4.8 d			

[†]Letters indicate Duncan's mean categories and are meant for comparison of CCP treatments within individual sampling dates only (Fall 2000, Spring 2002, Fall 2002).

10 g kg⁻¹ application rate by April 2002, and only the 40 g kg⁻¹ FGD treatment continued to differ from the control by the end of the study. In the case of FBC, significant differences in WEP were only observed at the 40 g kg⁻¹ rate, but these differences persisted across the entire study period. However, for ARA soil WEP was significantly less than the control in October 2000 and September 2002 at the 40 g kg⁻¹ rate.

The persistent influence of FGD and FBC on soil WEP in the 15-cm-deep samples over the 3-year study contrasted with the 1-year period during which the CCPs appeared to affect dissolved P in runoff. Differences in WEP and runoff dissolved-P trends likely represent discrepancies in the effective depth of interaction between runoff water (<5 cm) and the soil-sampling depth (15 cm). Sharpley (1985) concluded that the upper 0.1 to 3.7 cm of soil served as the source of dissolved P to runoff. Both CCP mixing depths and soil-sampling depths were deeper than the effective depth of interaction of the plot soils. Thus, changes in soil properties within the effective depth of interaction, such as those caused by erosion of CCPs from the soil surface, may not have been detected in the 15-cm-deep samples obtained in this study and regularly used for agronomic interpretation.

Trends in soil pH shed some light on differences in WEP observed among CCPs. For FGD, which had the greatest and longest-lasting effects on WEP, average soil pH was either significantly lower or not significantly different from the control (Table 3). Stout, Sharpley, and Pionke (1998) and Stout, Sharpley, and Landa (2000) found that the addition of FGD to soil significantly lowered pH, while Callahan et al. (2002) found FGD to reduce pH in only one of four acidic soils. At a low soil pH, such as that found in this study, the displacement of Al and Fe from cation-exchange sites and ensuing formation of insoluble Al and Fe phosphates would likely be the major mechanism by which FGD lowered soil WEP concentration. In addition, acidification may have increased the anion exchange capacity, hence P-sorption capacity, of amphoteric minerals in the soil (McBride 1994). In contrast with FGD, application of FBC significantly increased soil pH (Table 3). Similarly to FBC, ARA also increased soil pH, but only in October 2000 and in April 2002 at the greatest application rates. At the high pH values induced by amending soils with FBC, and to a lesser extent, ARA, Ca-phosphate formation likely played a role in decreasing WEP.

Conclusions

Results of this study indicate a limited, temporary impact of CCPs on dissolved P runoff from soils under continual corn production. Two CCPs, FBC and FGD, proved effective in decreasing WEP in soils to which they were applied, with effects persisting from 1–3 years, depending upon rate of application. All CCPs significantly lowered concentrations of dissolved P in runoff during the first year of the study, with FBC and FGD being the most effective. However, total P losses were unaffected by CCP application, probably because particulate P in runoff was the dominant form of P in runoff (dissolved P accounted for only 9–23% of total P in runoff in the first year of the study). Perhaps because of erosion of CCPs from the soil surface, the effect of CCPs on dissolved P in runoff did not persist beyond the first year. Although erosion rates at the site were substantial (0.63–1.47 Mg ha⁻¹), they were not uncharacteristically high for the area. Clearly, to be effective, CCPs must be used in a context where dissolved P constitutes the primary form of P in runoff and where erosion is minimized.

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