

# Reducing phosphorus export from croplands with FBC fly ash and FGD gypsum

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## Abstract

Excessive soil phosphorus levels cause high concentrations of water-soluble phosphorus in soil, thereby increasing the potential for phosphorus export to streams. Converting water-soluble phosphorus to less soluble forms with lime or calcium-containing coal combustion byproducts can reduce the release of soil phosphorus to surface runoff. A typical agricultural soil at excessive soil phosphorus levels was incubated with four treatments (0 to 20 g kg<sup>-1</sup>) of fluidized-bed combustion fly ash (FBC) and a flue-gas desulfurization (FGD) byproduct. A 10 g kg<sup>-1</sup> application of FBC and FGD to soil reduced the concentration of water-soluble phosphorus by 60% and 50%, respectively. Projection of these results over an agricultural watershed indicates that treating only 4% of the watershed can reduce the loss of water-soluble phosphorus by 30%. Published by Elsevier Science Ltd.

*Keywords:* Fluidized-bed combustion; Flue-gas desulfurization; Non-point source pollution

## 1. Introduction

Phosphorus enrichment of streams, lakes and freshwater portions of estuaries, such as Chesapeake Bay [1], is often the cause of algae blooms in these water bodies. A major source of such phosphorus enrichment can be surface runoff from croplands that have high levels of soil phosphorus. In the northeast USA, the majority of soil samples analyzed in 1990 by state soil testing laboratories for phosphorus exceeded phosphorus levels needed for plant production [2]. These high phosphorus levels increase the amount of water-soluble phosphorus in the soil, thereby increasing the potential for phosphorus export in surface runoff to streams [3, 4]. One way of controlling the release of soil phosphorus to surface runoff is to reduce its solubility by precipitation with other elements such as calcium, iron and aluminum [5]. Clean coal technology byproducts, such as fluidized-bed combustion (FBC) fly ash and flue-gas desulfurization (FGD) gypsum, are sources of elements and compounds that can precipitate phosphorus in soil.

Research has shown that FBC and FGD byproducts can provide an agronomic benefit by increasing soil pH, reducing surface runoff volumes and reducing the effects of subsoil acidity, and present no detrimental environmental effects when used at recommended rates [6–8]. Therefore,

the purpose of our research was to determine if these byproducts, as a source of calcium and lime, would reduce the amount of water-soluble phosphorus in the soil, thereby reducing the potential for phosphorus export into streams and lakes.

This paper presents the results from two experiments: (1) a laboratory equilibration that determined the mechanisms by which FGD and FBC byproducts reduce water-soluble phosphorus concentrations in the soil, and (2) a computer simulation to determine the effectiveness of FGD and FBC byproducts for reducing phosphorus exported in surface runoff from an agricultural watershed. These two experiments are part of a larger study incorporating different soils, plant responses, and plot and watershed runoff experiments.

## 2. Materials and methods

### 2.1. Equilibration study

The Ap horizon of a Berks shaley silt loam (Typic Dystrochrept, loamy-skeletal, mixed, mesic) was collected from a central Pennsylvania farm, air-dried and sieved (2 mm). The Berks series, with approximately 1 million acres mapped in Pennsylvania alone, is representative of the shale-derived soils that make up the bulk of the high-phosphorus agricultural soils in the animal-producing areas

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Table 1

Selected components of flue-gas desulfurization byproduct (FGD) and fluidized-bed combustion fly ash (FBC) used

Parameter	FGD	FBC
P (g kg <sup>-1</sup> )	0.0	0.3
Ca (g kg <sup>-1</sup> )	258	87
Calcium sulfate (g kg <sup>-1</sup> )	> 950	100
CaCO <sub>3</sub> equivalent (g kg <sup>-1</sup> )	< 10	310
Al (g kg <sup>-1</sup> )	0.1	22.1
Fe (g kg <sup>-1</sup> )	0.3	31.9
S (g kg <sup>-1</sup> )	220	34.2
pH ( - log H <sup>+</sup> )	8.3	12.1

of Pennsylvania and neighboring states [9]. Because of long-term lime, fertilizer and manure applications, the fertility of this soil was high (pH = 7.2; and 414, 611, 457 and 3720 kg ha<sup>-1</sup> of Mehlich-III extractable phosphorus, potassium, magnesium and calcium, respectively), and the organic matter content was 64.5 g kg<sup>-1</sup>. These soil fertility levels are representative of those on many farms of the northeastern United States that have high animal populations [10].

Two coal combustion byproducts were used (Table 1): FBC fly ash and forced oxidation FGD gypsum. Four rates of the byproducts (0, 5, 10 and 20 g kg<sup>-1</sup>) were mixed thoroughly with four 100 g replicate soil samples, which were moistened with distilled water. Excess water was allowed to drain for 48 h to approximately a 50% w/w moisture content, and the samples then placed in a 500 ml polyethylene bag and sealed with a head space of about 400 ml above the moistened soil. The samples were then allowed to incubate at ambient temperature for 21 days. After incubation, the soil samples were air-dried and stored for chemical analysis. The 10 g kg<sup>-1</sup> soil treatment approximates a land application of 3 mt ha<sup>-1</sup> needed to treat the top 2.5 cm of soil [4].

The treated soil was analyzed for water-soluble phosphorus [11], plant-available Mehlich-III phosphorus [16], and four fractions of inorganic phosphorus [12]. These inorganic phosphorus fractions are subsequently referred to as resin phosphorus (biologically available), NaHCO<sub>3</sub> phosphorus (biologically available), NaOH phosphorus (amorphous and some crystalline aluminum and iron phosphates), and HCl phosphorus (relatively stable calcium-bound). All phosphorus data were analyzed using the ANOVA and GLM procedures in SAS [13]. Use of the word 'significant' in the discussion indicates a probability level of 0.05.

Table 2

Observed water-soluble phosphorus concentrations within fields

Corn field (mg l <sup>-1</sup> )	3.45–17.3
Soybean field (mg l <sup>-1</sup> )	4.60–18.4
Rest of watershed (average) (mg l <sup>-1</sup> )	< 1

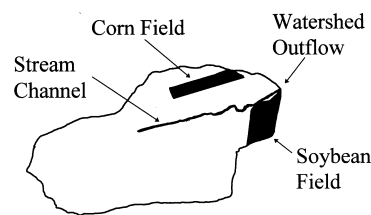


Fig. 1. FD-36 experimental watershed.

## 2.2. Runoff prediction

The AGNPS (AGricultural NonPoint Source) watershed model [14] was used to project the effect of byproduct treatment on phosphorus export from a watershed. AGNPS is an event-based model that simulates surface runoff, sediment and nutrient transport from agricultural watersheds. AGNPS operates on a cell basis that makes it possible to analyze discrete areas (fields) within a watershed. Routing is done in a stepwise manner, enabling the user to examine outputs at any point along the flow path. The nutrient transport module of AGNPS is divided into two parts, one handling soluble nutrients and the other handling sediment-attached nutrients.

An AGNPS data set was built for a 40 ha east-central Pennsylvania agricultural watershed (FD-36). The watershed is about 70% cropland and 30% woodland [15]. Soil and water-soluble phosphorus levels were obtained from a 30 m grid sampling. Fertilization levels and management practices were obtained from a farmer survey. AGNPS was then run and calibrated for an actual 51 mm, 14 h storm.

To determine the areas potentially contributing large amounts of phosphorus to streamflow, the phosphorus output of each cell in the watershed was charted. Two

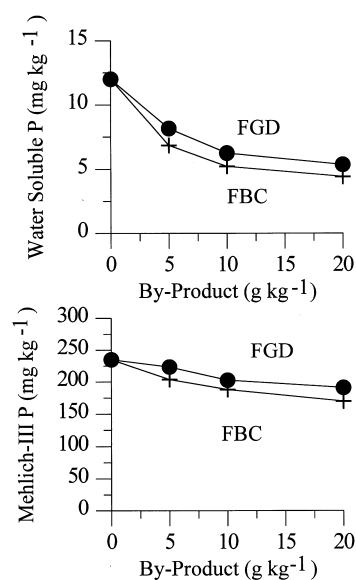


Fig. 2. Effect of FBC and FGD treatments on water-soluble phosphorus and Mehlich-III phosphorus contents of soil.

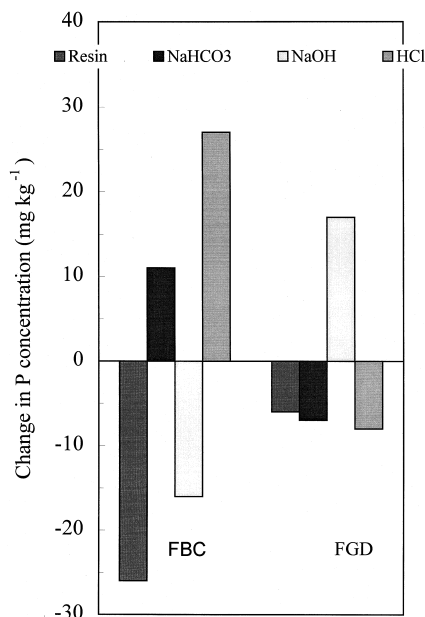


Fig. 3. Changes in inorganic phosphorus fractions at the 10 g kg<sup>-1</sup> treatment of FBC fly ash or FGD gypsum.

areas were shown to have higher soil phosphorus concentrations than the rest of the watershed (Table 2). The areas corresponded to a corn field (about 3% of the watershed area) and a soybean field (about 4% of the watershed area) (Fig. 1).

To simulate treating these areas with 10 g kg<sup>-1</sup> of either FBC or FGD byproducts, parameter estimates for the various phosphorus pools in the model (soil phosphorus, pore-water phosphorus and fertilizer phosphorus) were changed in accordance with the results of the incubation experiment (Fig. 2). Accordingly, the soil phosphorus pool, which was estimated by the Mehlich-III test, was reduced by 10%; while the pore water and fertilizer phosphorus pools, being reflective of water-soluble phosphorus, were reduced by 50%.

### 3. Results and discussion

Both the FBC and FGD materials reduced water-soluble phosphorus concentrations (Fig. 2, upper) in the soil samples. The effect of these materials was greatest up to

Table 3  
Simulated water-soluble phosphorus concentrations in surface runoff and percent phosphorus reductions at the watershed outlet

	P concentration (mg l <sup>-1</sup> )	% Reduction
Before byproduct treatment	0.10 <sup>a</sup>	—
Treatment on corn field	0.10	0.0
Treatment on soybean field	0.07	30.0

<sup>a</sup> Mean measured water-soluble phosphorus concentration (August to November, 1996) was 0.11 mg l<sup>-1</sup>.

the 10 g kg<sup>-1</sup> rate. Beyond this application rate the effect of these byproducts on water-soluble phosphorus concentration was diminished. At the 10 g kg<sup>-1</sup> application rate, FBC and FGD decreased the concentration of water-soluble phosphorus significantly by about 60% and 50%, respectively (Fig. 2, upper). Although both byproducts significantly decreased water-soluble phosphorus, neither reduced Mehlich-III phosphorus below 30 mg kg<sup>-1</sup>, the level where crop production would suffer (Fig. 2, lower) [16].

Although both byproducts reduced water-soluble phosphorus and Mehlich III phosphorus, the mechanisms by which they reduced these forms of soil phosphorus were different. The neutralizing capacity of FBC increased soil pH to 8.0, the level where phosphorus would be transformed to more basic calcium phosphates. Neither water nor Mehlich-III solution efficiently extracts these forms of phosphate. In contrast to FBC, the CaSO<sub>4</sub> in the FGD displaces H<sup>+</sup> from weakly acidic organic groups and clay surfaces, or generates H<sup>+</sup> by displacing Al<sup>3+</sup> and Fe<sup>3+</sup> oxides from the soil exchange complex [17]. The added H<sup>+</sup> reacted with soluble phosphorus to form phosphorus compounds not readily extracted with either water or Mehlich III. This is evidenced by the effect of FBC and FGD on soil inorganic phosphorus fractions (Fig. 3).

Amendment with FBC resulted in a shift from readily available resin phosphorus and less available NaOH-extractable iron- and aluminum-bound phosphorus fractions to HCl-extractable calcium-bound phosphorus (Fig. 3). This indicates that the neutralizing capacity of FBC is the primary factor and the Ca<sup>2+</sup> content the secondary factor in shifting a sizable portion of the soil phosphorus to the calcium-bound phosphorus fraction. In contrast to FBC, FGD addition resulted in a shift to NaOH-extractable iron- and aluminum-bound phosphorus from the other fractions. The controlling factor is the Ca<sup>2+</sup> addition which may have displaced Al<sup>3+</sup> or Fe<sup>3+</sup> into the soil solution, contributing to a decrease in soil pH and the conversion of resin and NaHCO<sub>3</sub>-extractable phosphorus to NaOH-extractable iron- and aluminum-bound phosphorus.

AGNPS predicted that phosphorus concentrations at the watershed outlet by treating the soybean field (4% watershed area) with either byproduct would reduce phosphorus export by 30% (Table 3). However, treating the corn field had no effect. This was because the two fields have different flow path characteristics and distances to the channel, and therefore contribute different amounts of surface runoff phosphorus to the watershed outlet. For example, the soybean field was comprised almost entirely of three subwatersheds which contributed surface runoff directly into the stream channel. On the other hand, surface runoff from the corn field either crosses three other fields before reaching the channel or percolates into the soil entering the stream channel as subsurface flow. In either case, soluble phosphorus in the surface runoff from the corn field would be mostly reduced by infiltration of the phosphorus-containing

surface runoff or by phosphorus removal from surface runoff by reaction with soils en route from field to stream. Therefore, the effect of byproduct treatment on reducing phosphorus runoff would be most effective on the hydraulically close soybean field than on the much more distant corn field [18].

From an agronomic perspective, the FGD would be the most desirable of the two byproducts to use on high-phosphorus soils where phosphorus loss in surface runoff is a concern. The FGD reduced water-soluble phosphorus with the little effect on plant-available phosphorus [5]. From an environmental perspective, FBC fly ashes may contain boron, selenium and other trace element concentrations that may be toxic to plants and animals if applied to cropland or pastures in large amounts. Therefore, loadings of these trace elements must be considered when developing a phosphorus export control program using FBC. In contrast, FGD byproducts are often high-quality gypsum containing very low levels of trace elements or other contaminants. Nevertheless, the long-term success of any remediation measure depends on the adoption of a sound nutrient management program. Application of these or any other amendments to reduce phosphorus export will not be effective over the long term if phosphorus continues to be applied in excess of crop requirements.

#### 4. Conclusions

The application of FBC or FGD byproducts to selected areas of an agricultural watershed has the potential to reduce the phosphorus enrichment of surface runoff without appreciably reducing plant-available phosphorus concentration levels. Use of FBC or FGD would allow soil phosphorus levels to be reduced through cropping over time, while controlling phosphorus export to surface waters in the short term. Clearly, this presumes that erosion from phosphorus source areas are controlled, otherwise the amendment effect on export of algal available phosphorus would be much less.

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