

# WATER-EXTRACTABLE PHOSPHORUS REDUCTION IN POULTRY LITTER WITH CALCIUM- AND IRON-RICH BYPRODUCT AMENDMENTS

G. K. Felton, K. J. Hughes, E. Russek-Cohen

**ABSTRACT.** *In the poultry producing regions of Delaware, Maryland, and Virginia, long-term application of poultry litter as the primary crop nitrogen source has resulted in elevated soil phosphorus (P) levels and is suspected of being a source of dissolved phosphorus in surface waters. Dissolved P is the most readily available form for algal uptake in receiving waters, and hence may disproportionately contribute to eutrophication. One potential solution to this problem that would allow farmers to continue land applying poultry litter is to amend manure with high P-affinity materials. Two high P-affinity materials produced in the titanium dioxide manufacturing process, secondary gypsum (SG) and filter cake (FC), were investigated as potential poultry litter amendments. Both are rich in iron, and SG also contains a significant quantity of calcium and sulfates, primarily in the form of gypsum. Laboratory experiments were conducted to investigate: (1) the appropriate ratio of litter to amendment, (2) the effect of 1, 2, and 4 week incubations on soluble P, and (3) the effect of amendments on poultry litter pH. Four treatments were investigated: (1) poultry litter only, and poultry litter amended with: (2) SG, (3) FC, and (4) a mixture (MIX) of SG and FC. The pH of the amended poultry litter decreased from an initial pH of 8.3 to a pH of 6.2 to 7.0. Amendment-to-litter ratio had the most profound impact on water-extractable phosphorus (WEP). All treatments significantly reduced WEP as compared to the control samples. Poultry litter to amendment mixtures at a 1:1 (mass basis) rate reduced WEP by 98%. The reduction dropped to 90% for the 2:1 mix, approximately 74% for the 4:1 mix, and 40% to 60% for the 8:1 mix.*

**Keywords.** *Filter cake, Secondary gypsum, Soluble phosphorus, Waste management.*

The Delmarva (Delaware, Maryland, and Virginia) peninsula region has intensive poultry production that generates approximately 703,500 Mg of poultry litter per year. Traditionally, land application of litter has provided both a fertilizer source and a means of disposal. However, long-term application of poultry litter as the primary crop nitrogen source has resulted in elevated soil phosphorus (P) levels and is a suspected cause of P in surface waters. Phosphorus in agricultural runoff, particularly from fields receiving animal manures in the Delmarva peninsula, has been linked to major pollution problems in the Chesapeake Bay region.

The principal mechanism by which P is lost from agricultural land is surface runoff (Coale, 2000). Phosphorus in surface runoff occurs in both dissolved and particulate

forms (Campbell and Edwards, 2001). Particulate P is associated with soil particles, and efforts to reduce soil erosion, such as no-till farming, significantly decrease particulate phosphorus in surface runoff (Sharpley et al., 1994). Dissolved (soluble) P consists mainly of inorganic P as orthophosphate (Sharpley et al., 1994), the form of phosphorus most readily available for algal uptake in receiving waters (Sonzogni et al., 1982; Walton and Lee, 1972).

Dissolved phosphorus concentrations in surface runoff from no-till fields can exceed those in runoff from fields with greater rates of soil erosion (Sharpley et al., 1992). Edwards and Daniel (1993) observed that dissolved P concentrations in surface runoff increased linearly with poultry litter application rates.

In conjunction with no-till farming, the practice of applying manure according to crop nitrogen requirements has also contributed to the problem of P losses to surface waters (Heathwaite et al., 2000). In soils, sorption sites and cations capable of precipitating soluble P are finite (Gilliam, 1995). Excess P in soils has been correlated with increased loss of P to surface waters (Sims et al., 2000; Carpenter et al., 1998; Sharpley et al., 1996). Sharpley (1995) and Pote et al. (1996) demonstrated that increased extractable soil P results in increased concentrations of dissolved P in surface runoff. Similarly, Sharpley and Moyer (2000) concluded that the potential for P loss via leaching and surface runoff from manure was most closely related to water-extractable phosphorus (WEP).

---

Article was submitted for review in June 2004; approved for publication by the Structures & Environment Division of ASAE in September 2004. Presented at the 2002 ASAE Annual Meeting as Paper No. 022269.

Use of manufacturer's names is to improve clarity only and does not constitute endorsement by the authors or the University of Maryland.

The authors are **Gary K. Felton**, ASAE Member Engineer, Assistant Professor, and **Kristen J. Hughes**, Research Assistant, Department of Biological Resources Engineering, University of Maryland, College Park, Maryland; and **Estelle Russek-Cohen**, Professor, Biometrics Program of Animal and Avian Sciences, University of Maryland, College Park, Maryland. **Corresponding author:** Dr. Gary K. Felton, Department of Biological Resources Engineering, University of Maryland, College Park, MD 20742-2315; phone: 301-405-8039; fax: 301-314-9023; e-mail: gfelton@umd.edu.

One potential solution to this problem that would allow farmers to continue applying poultry litter is to amend manure with high P-affinity materials. Metals, such as aluminum, iron, and calcium, can form insoluble, stable, metal-P complexes. Alum (aluminum sulfate) has the ability to reduce water-soluble P in poultry litter in both laboratory and field experiments (Moore and Miller, 1994; Shreeve et al., 1995; Moore et al., 1999). Moore and Miller (1994) also demonstrated, using laboratory experiments, that iron and calcium compounds were capable of reducing P solubility in poultry litter. Peters and Basta (1996) showed a reduction of bioavailable (soluble) P in soils using alum hydrosolids (a byproduct of drinking water treatment), cement kiln dust (rich in Ca oxides), and treated bauxite red mud (a byproduct of the aluminum industry that contains Al and Fe oxides and Ca) as soil amendments. Coale et al. (1994) reported that gypsum (calcium sulfate) amendments to organic soils (Histosols) resulted in long-lasting reduction of soluble P in soil leachate.

As noted by Moore and Miller (1994), poultry production provides an ideal setting for adding chemical amendments to animal waste. Poultry litter, which typically contains greater than 2000 mg kg<sup>-1</sup> of water-soluble P, consists of both poultry manure and bedding material (sawdust or wood shavings in Maryland), which is collected periodically and land applied. Iron, aluminum, and calcium amendments can increase the retention of P in much the same way as P is naturally retained in soils, a factor that is particularly important with surface-applied manure. An additional benefit of amendments is that iron and aluminum compounds such as ferric chloride, ferric sulfate, and aluminum sulfate (alum) reduce the volatilization of ammonia (Moore et al., 1999), thereby retaining more nitrogen for crop growth and allowing less nitrogen to escape to the atmosphere. One of the mechanisms for this effect involves the reaction of NH<sub>4</sub><sup>+</sup> with sulfate ions to form ammonium sulfate, a water-soluble fertilizer.

Previous research on secondary gypsum (SG) as a soil amendment has been reported by Offiah (1990), Offiah and Fanning (1994), Peacock and Rimmer (2000), and Hughes (2000). Offiah and Fanning (1994) investigated the potential for SG to neutralize acid sulfate soils and concluded that it was an efficient liming material. Peacock and Rimmer (2000) performed soil column dissolution experiments to evaluate SG as a sulfate source for soil amendments. They found that SG in a powder form had a high phosphate sorption capacity. Hughes (2000) studied the P sorption capacity of SG and reported that it had a very high P affinity at both neutral and alkaline pH levels (24 g P kg<sup>-1</sup> and 19 g P kg<sup>-1</sup>, respectively) and that more than 99% of P sorbed by SG was retained in desorption experiments with final pH ranges between 3.0 and 6.0.

An iron-rich residue called filter cake (FC) has also been investigated as a potential poultry litter and soil amendment for the purpose of reducing water-soluble P. Peacock and Rimmer (2000) investigated FC and found a considerably lower phosphate sorption capacity than they found for SG. Codling et al. (2000) found from laboratory incubation studies that FC added to poultry litter at 100 g kg<sup>-1</sup> reduced soluble P by 43%, 42%, and 62% for 2, 4, and 7 weeks of incubation, respectively. Dao et al. (2001) also investigated FC at an amendment rate of 200 g kg<sup>-1</sup> of poultry manure, to which wood chips were also added as a bulking agent. After

composting, dissolved P concentrations were reduced by 90% compared to the unamended control. Both Codling et al. (2000) and Dao et al. (2001) compared results with FC to aluminum-based byproducts from water treatment, although the material was obtained from two different sources. At 100 g kg<sup>-1</sup>, Codling et al. (2000) found that the aluminum-based water treatment residual was more efficient than FC in reducing soluble P, while Dao et al. (2001), using 590 g kg<sup>-1</sup>, reported the opposite. The difference in these reported results for both FC and aluminum-based water treatment residuals could be a factor of the amendment rate, the methods (composting vs. incubation), or the source of poultry litter and amendments.

While Moore et al. (1999) advocated alum as an amendment, we are investigating two materials rich in iron: SG and FC. Secondary gypsum also contains a significant quantity of calcium and sulfates, primarily in the form of gypsum (CaSO<sub>4</sub>). These materials are generated by two different titanium dioxide manufacturing processes and have the potential to be less expensive than alum. It is clear that SG has an affinity for P, and FC reduces soluble P. We examined both amendments to determine the appropriate ratio to reduce the soluble P to near zero, but to also make sure that we do not overdose the litter, which might result in a P deficiency in the receiving soil. The two amendments originate in two different processes with different costs and benefits, so we wish to examine their performance independently and as a mixture.

The objectives of this research are to: (1) determine whether SG and FC, either separately or in combination, are effective in reducing soluble P in poultry litter; (2) determine the appropriate poultry litter amendment rate for SG, FC, and a 50% combination (by weight) of the two; and (3) determine the effect of incubation time on soluble P reduction in amended poultry litter.

## MATERIALS AND METHODS

### AMENDMENT CHARACTERIZATION

Secondary gypsum was obtained from Millennium Inorganic Chemicals, Inc. (Baltimore, Md.), and FC was obtained from Millennium Inorganic Chemicals, Inc. (Ashtabula, Ohio). The SG and FC, which both have an initial consistency similar to that of damp clay, were dried at 104 °C for 24 h and then sieved through a 2 mm sieve. After drying and sieving, both materials had a powder-like consistency.

Inductively coupled plasma emission spectrometry (ICPES) was used to determine total calcium, iron, and sulfur in the amendments (U.S. EPA, 1996). Ammonium-N was determined by MgO distillation (AOAC, 1965). Total N was determined using a Leco CHN 600 combustion analyzer, as described by Campbell (1992). Total P was determined using perchloric acid/nitric acid digestion (Walsh, 1971), followed by analysis with a Technicon Auto-Analyzer using colorimetry (Flannery and Markus, 1980).

### POULTRY LITTER CHARACTERIZATION

Fresh poultry (*Gallus gallus domesticus*) litter was obtained from a broiler house on the eastern shore of Maryland. The litter had been used to grow out three flocks in a house measuring 183 × 12 m with approximately 30,000 birds per flock. Sawdust was used as the original

bedding material. In the laboratory, the poultry litter was refrigerated at 4°C until used. To ensure homogeneity, the poultry litter was mixed for 6 h in a concrete mixer and sieved through a 2 mm sieve. Moisture content was determined gravimetrically by drying five samples in a forced-draft oven at 104°C for 24 h. Ammonium-N was determined by MgO distillation (AOAC, 1965). Total N was determined using a Leco CHN 600 combustion analyzer, as described by Campbell (1992). Total P was determined using perchloric acid/nitric acid digestion (Walsh, 1971), followed by analysis with a Technicon Auto-Analyzer using colorimetry (Flannery and Markus, 1980).

## EXPERIMENTAL DESIGN

Moore and Miller (1994) used laboratory incubation experiments to examine the effects of various poultry litter amendments on soluble P. Our research utilized methods from their work so as to compare results from SG and FC with those previously reported. We extend this concept by first using SG with the inherent variability of a commercially produced product, and second, we extend incubation times to begin to investigate stability questions.

Four treatments were investigated: (1) poultry litter only, and poultry litter amended with: (2) SG, (3) FC, and (4) MIX, a mixture of SG and FC (50/50). All amendments were dried for 24 h at 104°C and sieved through a 2 mm sieve. Each amendment was investigated using four poultry litter-to-amendment dilutions (dry mass to dry mass) of 1:1, 2:1, 4:1, and 8:1, which correspond to 1000, 500, 250, and 125 g of amendment per kg of poultry litter. Because amendment treatments reduced the percentage mass of poultry litter in analyzed samples, water-extractable phosphorus results were adjusted to reflect the value of P extracted based on the actual mass of poultry litter in the sample analyzed. To determine if incubation time was a significant factor on soluble P level and pH, the four dilutions were subjected to three incubation time periods: 1, 2, and 4 weeks. The poultry litter only was used as a control, and because subsequent initial phosphorus reduction calculations were based on this control, ten replications were used for each time period. Six replicates were used for each treatment with amended poultry litter. Prepared amendments were weighed into 250 mL glass amber jars with Teflon lids, labeled, sealed, and kept at room temperature until poultry litter was added.

## INCUBATIONS

To each jar (250 mL, amber glass), the appropriate weight of amendment and 29 g of fresh poultry litter (the approximate wet weight equivalent of 20 g of dry poultry litter) was added. All jars were mixed by shaking (by hand) for 30 s/jar. Then, to obtain a total moisture content of 32.2% (the moisture content of the poultry litter control treatments), distilled water was added to each jar that received amendments to raise the amendment mix to a final moisture content of 32.2%. After water was added, each jar was mixed using a spatula, and sealed.

Prepared jars were then incubated in the dark at 25°C for the specified time period of 1, 2, or 4 weeks. After the incubation time period was completed, jars were removed, unsealed, and dried in a forced-draft oven at 60°C for 48 h. Samples were then sieved through a 2 mm mesh sieve and analyzed for pH and water-soluble P.

## WATER-EXTRACTABLE PHOSPHORUS

Sharpley and Moyer (2000) concluded that the potential for P loss via leaching and surface runoff from manure was most closely related to WEP. Hence, soluble P associated with the samples was estimated using a WEP analysis conducted according to methods given by Self-Davis et al. (2000). Specifically, 2 g of dried and sieved material was placed in a 50 mL centrifuge tube to which 20 mL of distilled water was added. Samples were agitated for 1 h on a reciprocating shaker and centrifuged at 6,000 rpm for 10 min. Solutions were then filtered through a 0.45 µm membrane filter. Filtrates were acidified to pH of 2.0 with concentrated HCl, and then frozen until analysis.

## STATISTICAL METHODS

P and pH data were analyzed using a 13 × 3 factorial design. The 13 treatments included four amendment-to-poultry litter dilutions (1:1, 2:1, 4:1, and 8:1) each for FC, SG, and the combination of 50% FC and 50% SG (weight basis), and the control (poultry litter only). The treatments were evaluated at 1 week, 2 weeks, and 4 weeks of incubation. All analysis was performed at 95% level of significance ( $\alpha = 0.05$ ).

Because of the controls, the data corresponded to a 3 × (4 × 3 + 1) design rather than a conventional factorial design. Contrast statements were used, which allowed us to assess amendment, ratio, and week, along with the corresponding two-way interactions. In addition, controls were compared to the mean of each amendment. Because variance appeared to vary with ratio, Proc Mixed was used to allow for heterogeneous variance even after the response variable was log-transformed.

A separate analysis was performed to calculate the ratio at which 50% of the WEP reduction was achieved. We only looked at week 2 data for this exercise. Two weeks is a reasonable time for a poultry litter stockpile to be left in a field prior to land application (although four weeks is also reasonable). We experimented with different regression models and selected log(WEP) versus ratio because that was the most linear model.

## RESULTS AND DISCUSSION

Poultry litter initial moisture content was 322 mg kg<sup>-1</sup>. Calcium, iron, sulfur, and nutrient contents of the two amendments and the poultry litter are listed in table 1. Mineralogical analysis indicated that SG contains 22% CaCO<sub>3</sub>, 48% CaSO<sub>4</sub>, and 16% Fe<sub>2</sub>O<sub>3</sub>, while FC contains 42% FeCl<sub>3</sub>, 12.4% CaCl<sub>2</sub>, and 11.7% AlCl<sub>3</sub>.

## TREATMENT EFFECT ON pH

The control (poultry litter) initially had a pH of 8.27. The pH dropped to 6.58 after week 1 and increased to 7.01 by

**Table 1. Concentration of relevant elements and compounds.**

Element	Secondary Gypsum (mg g <sup>-1</sup> )	Filter Cake (mg g <sup>-1</sup> )	Poultry Litter (mg g <sup>-1</sup> )
Ca	231	48	13
Fe	111	189	19
S	126	2	7
NH <sub>4</sub> -N	0	0	9
Total N	0	0	32
P <sub>2</sub> O <sub>5</sub>	0	0	27

week 4. Moore and Miller (1994) found similar changes over a one-week incubation (initial pH 8.2, decreased to 7.2). At these pH levels, calcite is relatively insoluble. However, anhydrite ( $\text{CaSO}_4$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) are considerably more soluble than calcite (Freeze and Cherry, 1979); hence  $\text{Ca}^{2+}$  will most likely be available in solution. As organic matter decays, carbonic acid is formed (Freeze and Cherry, 1979), which drives the pH down. As the microbes consume nutrients, the population shifts, the moisture content changes, the amount of feedstock changes, metabolic by-products accumulate, and the  $\text{CO}_2$  and  $\text{O}_2$  content in the jar changes. The increase in pH at week 2 is likely attributable to the dynamic balance between the  $\text{Ca}^{2+}$  in solution and the changing microbial activity that occurred during the incubation period.

Average pH values and standard errors at week 1, week 2, and week 4 for all treatments are listed in table 2. An ANOVA (SAS, 1999) was performed to examine relationships between pH and the type of amendment, the concentration of amendment, and the incubation time. All three factors were significant. Two 2-way interactions affected pH ( $p < 0.05$ ): type of amendment  $\times$  concentration, and type of amendment  $\times$  time.

Litter amended with SG at a 1:1 ratio maintained pH at approximately 6.80 throughout the four-week incubation period. As SG concentration decreased (2:1, 4:1, 8:1), the pH was reduced to 6.2–6.4. These lower pH values were statistically ( $\alpha = 0.05$ ) lower than the control pH values of the corresponding week. Higher concentrations of SG (1:1, 2:1) resulted in pH similar to the control, while lower concentrations of SG (4:1, 8:1) depressed pH beyond the control pH.

A plot (not shown) suggested that the control and the FC treatment may lead to similar pH results. As with the control, the pH of FC amended litter increased with time. A linear regression was performed on pH vs. FC concentration. An F-test ( $\alpha = 0.05$ ) showed that FC concentration was not a significant predictor of pH, but amendment concentration was a significant predictor for SG-amended litter and MIX-amended litter. The means of the control and FC were then tested to determine if FC had any effect on pH. A t-test (McCuen, 1985) showed that there was a significant difference between mean pH values of the control treatment and the FC treatment. Hence, the presence of FC was significant, but the concentration did not affect pH.

Significant differences in pH may not be agronomically relevant, because all treatments had final pH values that

ranged from 6.1 to 7.0. The primary importance of these results is related to ammonia ( $\text{NH}_3$ ) volatilization. All treatments, including incubation alone, resulted in a significant decrease in litter pH to a range that would be expected to reduce ammonia volatilization. Volatilization of ammonia in land-applied poultry litter reduces N availability to crops as well as contributing to atmospheric pollution. Carr et al. (1990) reported that ammonia volatilization increased with increasing pH. Specifically, they observed that at constant ventilation rates, very little ammonia was produced in poultry litter with pH values below 7.5, while increasing pH resulted in an exponentially increasing ammonia evolution rate. Moore et al. (1999) treated poultry litter with alum, which decreases litter pH, and reported a significant decrease in volatile ammonia concentrations. For all concentrations except 1:1, pH from SG treatment was lower than pH from FC treatment.

### TREATMENT EFFECTS ON WEP

The control WEP averaged 3830 mg P  $\text{kg}^{-1}$  with a standard deviation of 789 mg P  $\text{kg}^{-1}$  and a coefficient of variation (CV) of 21%. This indicates that the WEP from poultry litter is variable, which should carry through to the results in the rest of the experiment. Because there was such variability, ten replicates were done for the control. The larger number of replicates was to reduce error due to variability when control averages were used to calculate percent reduction in WEP.

One data point was suspect. Replicate 1 for FC, week 1, ratio 2:1 had a value of 2734 mg P  $\text{kg}^{-1}$ . Records from the water analysis laboratory indicated that this was a correct analysis, but records from the sample preparation were not so clear. The other five values ranged from 300 to 600 mg P  $\text{kg}^{-1}$ , with an average of 452 mg P  $\text{kg}^{-1}$ . With replicate 1 included, the CV was 102%, while the CV was 25% with replicate 1 omitted. Omitting replicate 1 put the CV much more in line with the CV of the control (21%). Therefore, it was assumed that this one outlier was due to sample preparation error and was discarded from the analysis.

A t-test (McCuen, 1985) on the control data indicated that week 2 samples contained significantly ( $\alpha = 0.05$ ) more WEP than either week 1 or week 4. Week 2 samples had 959 mg/kg higher WEP, or 27% higher WEP. Similar results were found by Codling et al. (2000). Increases can probably be attributed to mineralization of organic P, but there is a simultaneous consumption by the microbial population, which can account for decreases in WEP. This trend was not seen in all ratios of litter to amendment, nor was it seen consistently in a particular type of amendment. However, the trend with time (low, high, low for week 1, 2, and 4, respectively) was evident for the 2:1 ratio with SG, the 8:1 ratio with SG, the 4:1 ratio with FC, and the 4:1 ratio with MIX. These changes in control WEP have a ramification for the reduction-in-WEP calculation because the average control WEP value is used to calculate percent reduction for each observation.

All treatments significantly reduced WEP as compared to the control samples for all incubation durations (fig. 1). Each control bar represents ten replications, and each treatment bar represents six replications. Standard errors ranged from 0.1% to 7.6% of full scale (5000 mg  $\text{kg}^{-1}$ ).

Figure 1 suggests that the amendment ratio dominates the WEP response. From the ANOVA (SAS, 1999), it was

**Table 2. Effect of treatment on final pH.**

Treatment	Rates	Week 1	Week 2	Week 4
Control	1:0	6.58 $\pm$ 0.08	6.92 $\pm$ 0.05	7.01 $\pm$ 0.03
SG	1:1	6.80 $\pm$ 0.08	6.73 $\pm$ 0.10	6.85 $\pm$ 0.07
	2:1	6.44 $\pm$ 0.05	6.30 $\pm$ 0.06	6.47 $\pm$ 0.07
	4:1	6.23 $\pm$ 0.02	6.20 $\pm$ 0.04	6.27 $\pm$ 0.02
	8:1	6.33 $\pm$ 0.01	6.17 $\pm$ 0.05	6.36 $\pm$ 0.01
FC	1:1	6.58 $\pm$ 0.06	6.64 $\pm$ 0.06	6.95 $\pm$ 0.04
	2:1	6.52 $\pm$ 0.05	6.58 $\pm$ 0.04	6.88 $\pm$ 0.04
	4:1	6.65 $\pm$ 0.02	6.61 $\pm$ 0.04	6.93 $\pm$ 0.02
	8:1	6.75 $\pm$ 0.05	6.78 $\pm$ 0.05	7.04 $\pm$ 0.02
MIX	1:1	6.61 $\pm$ 0.10	6.72 $\pm$ 0.06	6.95 $\pm$ 0.04
	2:1	6.41 $\pm$ 0.03	6.38 $\pm$ 0.08	6.57 $\pm$ 0.05
	4:1	6.34 $\pm$ 0.01	6.21 $\pm$ 0.04	6.41 $\pm$ 0.03
	8:1	6.36 $\pm$ 0.05	6.38 $\pm$ 0.04	6.52 $\pm$ 0.04

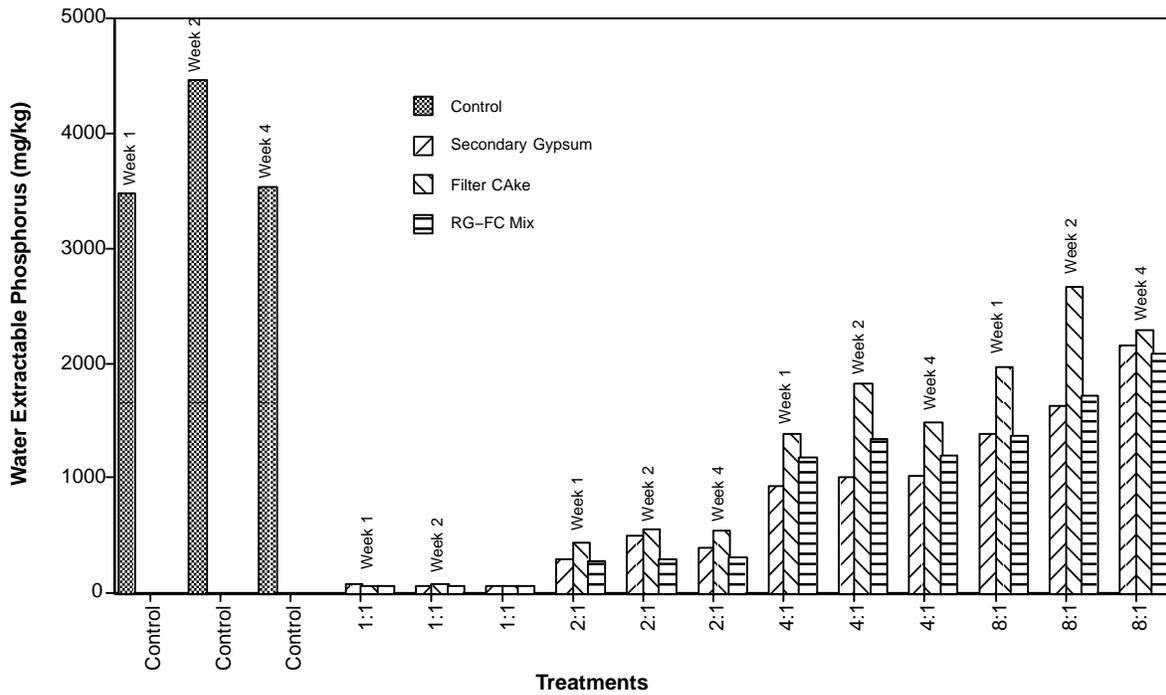


Figure 1. Water-extractable phosphorus ( $\text{mg P kg}^{-1}$  poultry litter) of treatments.

determined that the time variable (week) was not a significant predictor of WEP, nor were there any two-way interactions involving week. There was not a significant three-way interaction. However, amendment type and ratio of litter-to-

amendment were both significant, as well as the two-way interaction between the two.

WEP and  $\log(\text{WEP})$  were plotted against the ratio,  $1/\text{ratio}$ , and  $\log(1/\text{ratio})$ . These plots suggested that the  $\log(\text{WEP})$  vs.

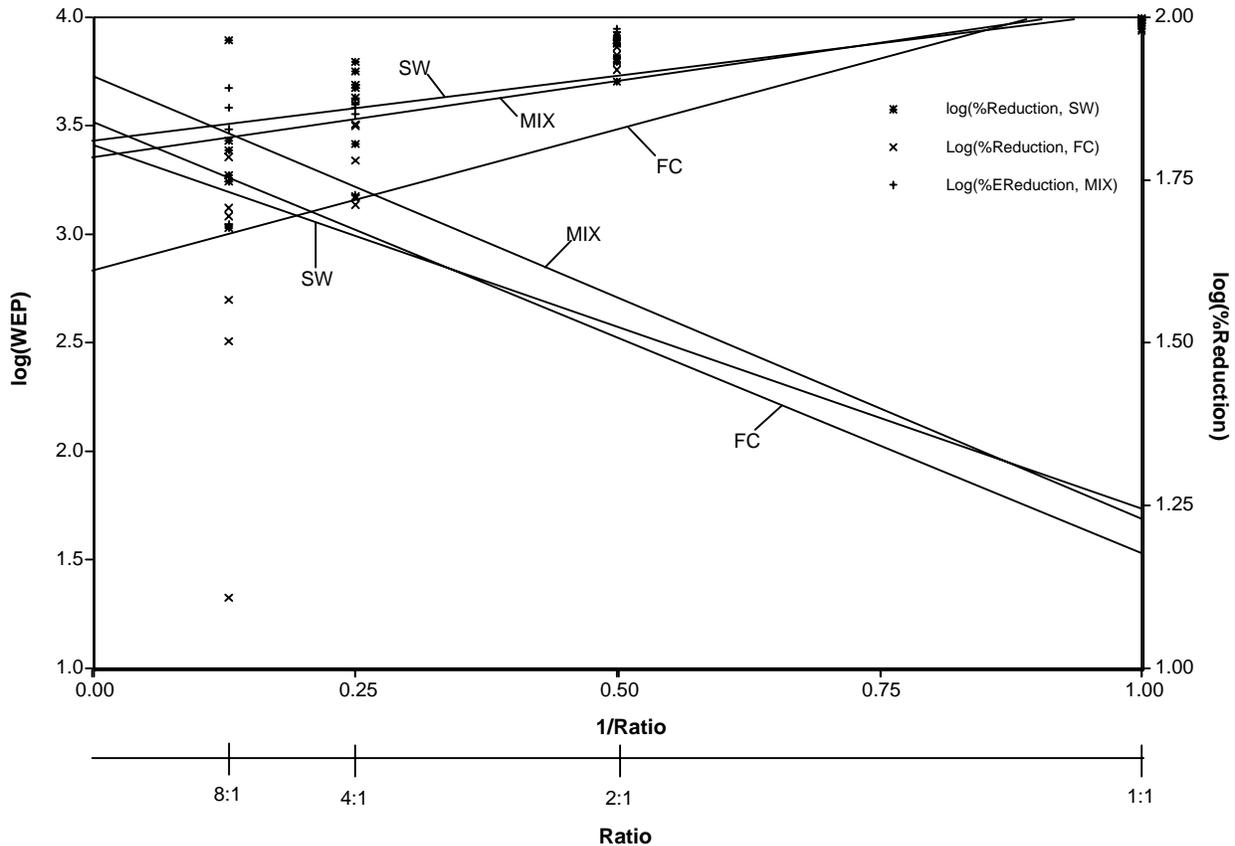


Figure 2. Linear regression lines relating water-extractable phosphorus to the litter-to-amendment ratio (negative slopes) and percent reduction from control (positive slopes).

1/ratio was the most linear relationship and that the variance in WEP was not at all homogeneous. Other curve forms were also fit to the data. Power curves and log curves fit some of the data better but made no sense because they predicted WEP reduction in excess of 100%. A quadratic curve not only predicted reduction in excess of 100%, but also decreased recent reduction when the concentration exceeded 1:1.

Hence, linear regressions (SAS, 1999) were developed for each type of amendment (SW, MIX, and FC) relating  $\log_{10}(\text{WEP})$  and the 1/ratio. The regression equations were of the following form:

$$\log_{10}(\text{WEP}) = b_0 + b_1 \left( \frac{1}{\text{ratio}} \right) \quad (1)$$

These lines are plotted in figure 2. There are no  $R^2$  values because it is not a legitimate measure of goodness-of-fit when variances are not homogeneous across the range of data. The regression coefficients for equation 1 are listed in table 3.

#### AMENDMENT RATIO SPECIFICATION

Figure 2 provides the linear regression lines that relate WEP to the poultry litter-to-amendment ratio and also presents the regression lines that relate percent reduction in soluble WEP to the poultry litter-to-amendment ratio. These relationships are of the form:

$$\log_{10}(\% \text{ reduction}) = b_0 + b_1 \left( \frac{1}{\text{ratio}} \right) \quad (2)$$

The regression coefficients are listed in table 3. For this relationship, the individual data points were also plotted to illustrate the nonhomogeneity in variance across the range of data. ANOVA (SAS, 1999) results indicate that the regression lines are significant ( $\alpha = 0.05$ ).

To obtain the appropriate ratio for a specified reduction, a problem known as the inverse regression problem (Draper and Smith, 1981) must be solved. Based on our regression models, we estimated the mean of  $\log(\text{WEP})$  at a specific ratio as:

$$\log_{10}(\text{WEP}) = b_0 + b_1 \left( \frac{1}{\text{ratio}} \right) \quad (3)$$

and the estimate of the mean of  $\overline{\log(\text{control})}$  is the log of the mean of the ten control values (control) at week 2. We solved for the ratio that satisfies:

$$\log_{10}(\overline{\text{WEP}}) - \log_{10}(\overline{\text{control}}) = \log_{10}(0.50) \quad (4)$$

We calculated an inverse prediction interval about the 50% reduction in WEP by a generalization of a method in Draper and Smith (1981). Specifically, we solved for the ratio that satisfied:

$$a + b \left( \frac{1}{\text{ratio}} \right) - \log_{10}(\overline{\text{control}}) = \log_{10}(0.50) \quad (5)$$

The regression (eq. 2) was solved using Proc Mixed (SAS, 1999) allowing for heterogeneous variation. The variance of equation 5 is:

$$\begin{aligned} & \overline{\overline{\text{Var}}(a)} + \left( \frac{1}{\text{ratio}} \right)^2 \overline{\overline{\text{Var}}(b)} \\ & + 2 \left( \frac{1}{\text{ratio}} \right) \overline{\overline{\text{Cov}}(a,b)} + \overline{\overline{\text{Var}}(\text{control})} \end{aligned} \quad (6)$$

where the double overbar symbols represent values that are determined by Proc Mixed, and  $\overline{\overline{\text{Var}}(\text{control})}$  is the variance of the ten control values divided by 10. The square root of the term represented by equation 6 is the standard error. We then solved for all doses in which:

$$\left| \frac{a + b \left( \frac{1}{\text{ratio}} \right) - \log_{10}(\overline{\text{control}}) - \log_{10}(0.50)}{\sqrt{\text{equation 6}}} \right| < 1.96 \quad (7)$$

By using  $\log_{10}(0.10)$  in place of  $\log_{10}(0.50)$ , we can solve for values of ratio that result in a 90% reduction. In cases where 50% reduction was not observed in the data, it was not possible to generate a prediction interval around the 50% reduction. In summary, determining the appropriate ratio to obtain a specific reduction requires the relatively straightforward solution of equations 1 or 2. Obtaining a confidence interval is more complex and requires obtaining the values to satisfy equation 7 using Proc Mixed (SAS, 1999).

#### SECONDARY GYPSUM

All amendment dilutions of the SG treatments were effective in reducing poultry litter WEP (fig. 1). For 1, 2, and 4 week incubations, the 1:1 amendment dilutions reduced soluble phosphorus by 98%, and the 2:1 dilution reduced soluble P by approximately 90%. The 4:1 dilution reduced soluble phosphorus in the range of 71% to 77%, while the 8:1 amendment dilutions decreased soluble P in the range of approximately 40% to 60%.

Although the mechanism by which SG reduces poultry litter P solubility is not precisely defined at the molecular level, previous research on SG suggests that both Ca and Fe oxides play an important role. Offiah (1990) used petrographic thin-section techniques to characterize the micromorphology of SG and determined that the  $\text{CaSO}_4$  occurred in the form of euhedral prismatic, transparent grains, while the aragonite ( $\text{CaCO}_3$ ) grains were microcrystalline in nature, and coated with Fe oxides.

Hughes (2000) analyzed soluble Ca and Fe in P sorption isotherm solutions and found that Ca concentrations averaged  $138 \text{ g kg}^{-1}$  in zero-P solutions and decreased to almost zero with increased inorganic P concentrations. These results indicated that a portion of the Ca present in SG was soluble and available for reaction with P. Iron was present in very low concentrations, which did not change with increased solution P. These results combined with Offiah's (1990) micromorphology results suggest that any soluble Ca associated

**Table 3. Regression coefficients for equations 2 and 3, specific to each type of amendment.**

Amendment Type	Equation 2		Equation 3	
	$b_0$	$b_1$	$b_0$	$b_1$
SW	3.4022	-1.6348	1.810	0.203
MIX	3.5419	-2.0836	1.787	0.236
FC	3.7115	-1.953	1.611	0.437

with SG may contribute to P removal via precipitation, as well as sorption onto calcite surfaces. Both SG and FC contain Fe and Ca. Calcium will react with P at pH greater than 10 to form hydroxyapatite (Metcalf and Eddy, 1991). Under our experimental conditions, it is not likely that this reaction occurred. However, P will precipitate with Fe in the following reaction:



Although the Fe oxides associated with SG most likely do not contribute to phosphorus removal via precipitation, they may remove P via sorption of P onto Fe oxide surfaces.

#### FILTER CAKE

FC amendments also resulted in a significant decrease in poultry litter WEP (fig. 1), ranging from greater than 98% (1:1) to approximately 40% (8:1). The 8:1 amendment results for WEP reduction (44%) are similar to those found by Codling et al. (2000), who reported a 43% P reduction for a 10:1 application rate after two weeks of incubation.

The mechanism by which the FC immobilizes P is most likely related to the high iron concentration, although the calcium and aluminum present in the material may also contribute. Metal analysis indicated that FC contains approximately 30% more Fe than SG. However, while the iron associated with SG is in the form of oxides (Offiah, 1990), which gives the SG a red color, ferric chloride ( $\text{FeCl}_3$ ) is the predominant form of iron in FC. Moore and Miller (1994) amended poultry litter with ferric chloride ( $\text{FeCl}_3$ ) at rates of 4:1, 5:1, 6.7:1, 10:1, and 20:1. As FC contains approximately 14% Fe, while laboratory-grade  $\text{FeCl}_3$  contains 34% by molecular weight, the 2:1 and 4:1 poultry litter to FC amendment rate in this experiment would closely correspond with the 5:1 and 10:1 poultry litter to  $\text{FeCl}_3$  rate in the Moore and Miller (1994) experiment. In both experiments, soluble P was measured as WEP, and treatments were incubated for one week; hence, the results are comparable. In this experiment, at the 2:1 and 4:1 amendment rates, the FC reduced WEP by approximately 76% and 60%, respectively. Moore and Miller (1994) reported a removal efficiency of greater than 90% for the 10:1 rate, while the 5:1 rate demonstrated a net increase in P solubility. However, in the Moore and Miller experiment, the reported values for pH at the higher rates approached 2, and they suggest that this pH effect may have resulted in increased P solubility via dissolution of Ca phosphates, acid hydrolysis of organic P, and/or decreased P adsorption by Fe compounds due to dissolution of Fe oxides and hydroxides in the low pH environment. They concluded that the P removal efficiency of  $\text{FeCl}_3$  may be increased if the pH of the litter had been maintained at a higher value. In this respect, the FC treatment, which, for the 2:1 and 4:1 amendment rates, had final pH values of 6.52 and 6.65, respectively (table 2), may have an advantage over  $\text{FeCl}_3$  amendments.

#### SG AND FC COMBINATION

MIX also resulted in significant reductions in WEP as compared to the control (fig. 1). The 1:1 and 2:1 dilutions reduced WEP by approximately 98% and by 91% to 92%, respectively. The 4:1 and 8:1 treatments reduced WEP by approximately 66% to 70% and 40% to 60%, respectively.

#### RAMIFICATIONS OF AMENDMENT RESULTS

As the amount of litter increased (increasing ratio), the variability increased. This was expected because of the variability in the poultry litter control. However, this has some ramifications for amendment utilization. First, the lower ratios (higher amendment concentration) have better predictability and are a better choice if a specific WEP reduction is necessary.

Next, the variability of litter extends to the source. In Maryland, sawdust and wood shavings are common litter materials. In Arkansas, rice hulls are a common litter material. Because different litter materials are variable, some testing to develop curves such as figure 2 would be necessary to develop appropriate amendment ratios for different materials, independent of the amendment.

In terms of practical application and agricultural management decisions, how the amendments compare with each other and with amendments investigated in previously published research is of interest. Overall, the three treatments in this study (SG, FC, and MIX) demonstrated similar performances with respect to WEP reduction. Although WEP removal efficiencies for FC-amended litter are generally less than the SG and MIX treatments (fig. 1), when amendment ratio and incubation time were held constant, there were relatively few significant differences between the three amendments. This is not surprising considering the similarity in performances of FC and SG.

Both SG and FC reduce WEP associated with poultry litter by 90% or more at dilutions of 2:1 or greater, which provides an environmental benefit. However, efficiencies at the field scale cannot be expected to be as high as laboratory results. Treatments in this study were thoroughly dried, sieved, and mixed; a thorough process that may not be replicable on a larger scale. Hence, field experiments are necessary to estimate field efficiencies.

A second concern deals with the utilization of any amendment designed to reduce WEP in manure in conjunction with regulations such as those implemented in Maryland. In Maryland, the Phosphorus Site Index (PSI) assessment (Maryland Cooperative Extension, 1999) is required for soils that test in the "excessive P" range for soil test phosphorus (STP). The PSI takes into consideration factors such as STP, soil type, fertilizer source and P availability, slope, buffer strips, runoff potential, and cropping methods to derive a final rating based on the potential for P loss to surface waters. The final rating is based on five categories (high risk to low risk) on which P application guidelines are based. A low risk rating allows the continued application of manure based on N requirements, while a medium to high risk rating indicates that P applications must either be limited to annual crop requirements or eliminated completely.

An important parameter in determining the P contribution of organic fertilizers is the phosphorus availability coefficient (PAC) of the fertilizer source assessment (Maryland Cooperative Extension, 1999). Amending poultry litter with P-fixing amendments such as SG and FC will reduce the PAC availability coefficient for the fertilizer source. While the use for manure amendments that reduce WEP may allow for greater flexibility in the application of poultry litter, the means for taking into account the effect of amendments on the PAC need to be incorporated into these regulations and communicated to nutrient managers.

## FUTURE WORK

The addition of large amounts (1.5 to 3.0 tons ac<sup>-1</sup>) of calcium found in the SG amendment will not have an adverse effect on Maryland Coastal Plain soils, which are typically sandy and acidic. However, the use of this concept on clayey soils or soils with pH above neutral should be investigated.

Because the amendment ratios were designed based on P content of the litter mix, crops should not experience P deprivation. As long as this treatment is applied to high-P soils, there should not be crop growth problems associated with P. However, field plot research is needed to verify WEP reduction under field conditions.

## CONCLUSION

The pH of the litter-amendment mix was between 6.2 and 7.0, which will help to reduce ammonia volatilization, but not as dramatically as alum. In general, length of incubation time did not have a significant effect on treatment effectiveness. All three amendments investigated (SG, FC, and MIX) were effective in reducing WEP in poultry litter. Although efficiencies of WEP removal by FC are generally less than the SG and MIX treatments, when amendment ratio and incubation time were held constant, there were relatively few significant differences between the three amendments. This experiment indicates that a 2:1 ratio for both SG and MIX, and approximately a 1.4:1 ratio for FC reduced WEP by 90%. This approach has the potential to significantly reduce the WEP leaving a field that has been treated with poultry litter. However, further research is needed to ensure that the amendments do not negatively impact crop growth.

## ACKNOWLEDGEMENTS

The authors are grateful to Millennium Inorganic Chemicals, Inc., and the Maryland Industrial Partnerships program for providing funding and supporting this project. We wish to thank Dr. Laurine Ottmar and Mr. Mike Robinson of Millennium Inorganic Chemicals, Inc., for their support and assistance during this project. We appreciate the assistance of Mr. Ted Andrews (Department of Biological Resources Engineering, University of Maryland) for his work on chemical analysis. Statistical analysis was aided and enhanced by Dr. Mary Christman (Biometrics Program of Animal and Avian Sciences, University of Maryland).

## REFERENCES

- AOAC. 1965. *Official Standards of Analysis*. Washington, D.C.: Association of Analytical Communities.
- Campbell, C. R. 1992. Determination of total nitrogen in plant tissue by combustion. In *Plant Analysis Reference Procedures for the Southern Region of the U.S. Southern Coop.*, 21–23. Res. Ser. Bulletin 368. Washington, D.C.: USDA.
- Campbell, K. L., and D. R. Edwards. 2001. Phosphorus and water quality impacts. In *Agricultural Nonpoint-Source Pollution*. W. F. Ritter and A. Shirmohammadi, eds. Boca, Raton, Fla.: Lewis Publishers.
- Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecol. Applic.* 8(3): 559–568.
- Carr, L. E., F. W. Wheaton, and L. W. Douglas. 1990. Empirical models to determine ammonia concentrations from broiler chicken litter. *Trans. ASAE* 33(4): 1337–1342.
- Coale, F. J. 2000. Phosphorus dynamics in soils of the Chesapeake Bay watershed. In *Agriculture and Phosphorus Management: The Chesapeake Bay*, 43–56. A. N. Sharpley, ed. Boca Raton, Fla.: Lewis Publishers.
- Coale, F. J., P. S. Porter, and W. Davis. 1994. Soil amendments for reducing phosphorus concentration of drainage water from histosols. *SSSA J.* 58(6): 1470–1475.
- Codling, E. E., R. L. Chaney, and C. L. Mulchi. 2000. Use of aluminum- and iron-rich residues to immobilize phosphorus in poultry litter and litter-amended soils. *J. Environ. Qual.* 29(6): 1924–1931.
- Dao, T. H., L. J. Sikora, A. Hamasaki, and R. L. Chaney. 2001. Manure phosphorus extractability as affected by aluminum- and iron by-products and aerobic composting. *J. Environ. Qual.* 30(5): 1693–1698.
- Draper, N., and H. Smith. 1981. *Applied Regression Analysis*, 47–51. 2nd ed. New York, N.Y.: Wiley Press.
- Edwards, D. R., and T. C. Daniel. 1993. Effects of poultry litter application rate and rainfall intensity on quality of runoff from fescue grass plots. *J. Environ. Qual.* 22(2): 361–365.
- Flannery, R. L., and D. K. Markus. 1980. Automated analysis of soil extracts for P, K, Ca, and Mg. *J. Assoc. Off. Anal. Chem.* 63: 779–787.
- Freeze, R. A., and J. A. Cherry. 1979. *Groundwater*. Englewood Cliffs, N.J.: Prentice-Hall.
- Gilliam, J. W. 1995. Phosphorus control strategies. *Ecol. Eng.* 5(2–3): 405–414.
- Heathwaite, L., A. Sharpely, and W. Gburek. 2000. A conceptual approach for integrating phosphorus and nitrogen management at watershed scales. *J. Environ. Qual.* 29(1): 158–166.
- Hughes, K. J. 2000. Potential for calcium by-products to remove phosphorus in dairy-waste treatment constructed wetlands. MS thesis. College Park, Md.: University of Maryland.
- Maryland Cooperative Extension. 1999. The Maryland Phosphorus Site Index: A Technical User's Guide (Version 1). College Park, Md.: University of Maryland.
- McCuen, R. H. 1985. *Statistical Methods for Engineers*, Chapter 8. Englewood Cliffs, N.J.: Prentice-Hall.
- Metcalf and Eddy. 1991. *Wastewater Engineering: Treatment, Disposal, Reuse*. Revised by G. Tcholoanoglous and F. L. Burton. 3rd ed. New York, N.Y.: McGraw-Hill.
- Moore, P. A., T. C. Daniel, and D. R. Edwards. 1999. Phosphorus runoff and improving poultry production with alum. *Poultry Sci.* 78: 692–698.
- Moore, P. A., and D. M. Miller. 1994. Decreasing phosphorus solubility in poultry litter with aluminum, calcium, and iron amendments. *J. Environ. Qual.* 23(2): 325–330.
- Offiah, O. 1990. Mineralogy, liming value, and possible vanadium hazard of SWAN-gypsum as soil material. PhD diss. College Park, Md.: University of Maryland.
- Offiah, O., and D. S. Fanning. 1994. Liming value determination of a calcareous, gypsiferous waste for acid sulfate soil. *J. Environ. Qual.* 23(2): 331–337.
- Peacock, S., and D. L. Rimmer. 2000. The suitability of an iron oxide-rich gypsum by-product as a soil amendment. *J. Environ. Qual.* 29(6): 1969–1975.
- Peters, J., and N. Basta. 1996. Reduction of excessive bioavailable phosphorus in soils by using municipal and industrial wastes. *J. Environ. Qual.* 25(6): 1236–1241.
- Pote, D. H., T. C. Daniel, A. N. Sharpley, P. A. Moore, D. R. Edwards, and D. J. Nichols. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *SSSA J.* 60(3): 855–859.
- SAS. 1999. SAS OnlineDoc. v8. Cary, N.C.: SAS Institute, Inc.
- Self-Davis, M. L., P. A. Moore, Jr., B. C. Joern. 2000. Determination of water and/or dilute salt extractable phosphorus.

- In *Methods of Phosphorus Analysis for Soils, Sediments, Residuals and Waters*. Southern Cooperative Series Bulletin No. 396. Southern Association of Agricultural Experiment Station Directors (SAAESD).
- Sharpley, A. N. 1995. Dependence of runoff phosphorus on extractable soil phosphorus. *J. Environ. Qual.* 24(5): 920–926.
- Sharpley, A. N., and B. Moyer. 2000. Phosphorus forms in manure and compost and their release during simulated rainfall. *J. Environ. Qual.* 29(5): 1462–1469.
- Sharpley, A. N., S. J. Smith, O. R. Jones, W. A. Berg, and G. A. Coleman. 1992. The transport of bioavailable phosphorus in agricultural runoff. *J. Environ. Qual.* 21(1): 30–35.
- Sharpley, A. N., S. C. Chapra, R. Wedepohl, J. T. Sims, T. C. Daniel, and K. R. Reddy. 1994. Managing agricultural phosphorus for protection of surface waters: Issues and options. *J. Environ. Qual.* 23(3): 437–451.
- Sharpley, A. N., T. C. Daniel, J. T. Sims, and D. H. Pote. 1996. Determining environmentally sound soil phosphorus levels. *J. Soil and Water Cons.* 51(2): 160–166.
- Shreeve, B. R., P. A. Moore, T. C. Daniel, D. R. Edwards, and D. M. Miller. 1995. Reduction in phosphorus in runoff from field applied poultry litter using chemical amendments. *J. Environ. Qual.* 24(1): 106–111.
- Sims, J. T., A. C. Edwards, O. F. Schoumans, and R. R. Simard. 2000. Integrating soil phosphorus testing into environmentally based agricultural management practices. *J. Environ. Qual.* 29(1): 60–71.
- Sonzogni, W. C., S. C. Chapra, D. E. Armstrong, and T. J. Logan. 1982. Bioavailability of phosphorus inputs to lakes. *J. Environ. Qual.* 11(4): 555–563.
- U.S. EPA. 1996. SW-846: Methods for Evaluating Solid Waste Physical/Chemical Methods, Part I. Method 6010B, “Inductively Coupled Plasma–Emission Spectrometry”, Revision 2, December 1996. EPA SW-846.3.3. Washington, D.C.: U.S. Environmental Protection Agency.
- Walsh, L. M. 1971. *Instrumental Methods for Analysis of Soils and Plant Tissue*. Madison, Wisc.: Soil Science Society of America.
- Walton, C. P., and G. F. Lee. 1972. A biological evaluation of the molybdenum blue method for orthophosphate analysis. *Tech. Int. Ver. Limnol.* 18: 676–684.

