Decreasing Phosphorus Solubility in Poultry Litter with Aluminum, Calcium, and Iron Amendments

P. A. Moore, Jr.* and D. M. Miller

ABSTRACT

Arkansas produces approximately one billion broilers (Gallus gallus domesticus) each year. Phosphorus runoff from fields receiving poultry litter is believed to be one of the primary factors affecting water quality in northwest Arkansas. Poultry litter contains 20 g P kg⁻¹, of which 2 g P kg⁻¹ is water soluble. The objective of this study was to determine if soluble P levels could be reduced in poultry litter with Al, Ca, and/or Fe amendments. Poultry litter was amended with alum, sodium aluminate, quick lime, slaked lime, calcitic limestone, dolomitic limestone, gypsum, ferrous chloride, ferric chloride, ferrous sulfate, and ferric sulfate, and incubated in the dark at 25 °C for 1 wk. The Ca treatments were tested with and without CaF₂ additions in an attempt to precipitate fluorapatite. At the end of the incubation period, the litter was extracted with deionized water and water soluble P determined. Water soluble P levels in the poultry litter were reduced from >2,000 mg P kg⁻¹ litter to <1 mg P kg⁻¹ litter with the addition of alum, quick lime, slaked lime, ferrous chloride, ferric chloride, ferrous sulfate, and ferric sulfate under favorable pH conditions. Gypsum and sodium aluminate reduced water soluble P levels by 50 to 60%. Calcitic and dolomitic limestone were less effective. The results of this study suggest that treating litter prior to field application with some of these compounds could significantly reduce the amount of soluble P in runoff from litter-amended pastures. Therefore, chemical additions to reduce soluble P in litter may be a best management practice in situations where eutrophication of adjacent water bodies due to P runoff has been identified. Preliminary calculations indicate that this practice may be economically feasible. More research is needed, however, to determine any beneficial and/or detrimental aspects of this practice.

Phosphorus is generally considered the limiting nutrient responsible for eutrophication in lakes and reservoirs, since certain algal species can obtain N from atmospheric sources. Tighter controls of point sources of P, such as municipal wastewater treatment plants, has resulted in decreased P loading from point sources into the aquatic environment in the last few decades. Improvement of water quality, however, has not always been observed when point source loads were reduced. Therefore, attention is currently being focused on nonpoint sources of P, such as agricultural runoff. One of the major sources of P runoff from agricultural lands is animal waste.

Several investigators have characterized P runoff from fields receiving poultry manure (Edwards and Daniel, 1993a,b; McLeod and Hegg, 1984; Westerman and Overcash, 1980; Westerman et al., 1983). The best information on P fixation has been provided by researchers studying wastewater treatment. In a review of Swedish wastewater treatment plants, Ulmgren (1975) found that when alum was used to precipitate P, the pH had to be lower than 6.4 to result in P concentrations of 0.8 mg P L⁻¹, whereas the pH needed to reach this concentration with lime was 11.5. He indicated that at a pH of 6.0, AlPO₄ solubility reaches a minimum (001 mg P L⁻¹). The Al/P mole ratios generally found in the precipitates were 1.5 to 2.5. Of the plants studied in Sweden, 33 used alum, 9 used quicklime (CaO), and 1 used ferric chloride. Treatment with these substances not only reduced P content in effluent water, but also decreased suspended solids, BOD, heavy metals, worm eggs, and parasites (Ulmgren, 1975).

Precipitation reactions for Al, Ca, and Fe phosphates are:


Abbreviations: BOD, biochemical oxygen demand; EC, electrical conductivity; APHA, American Public Health Association; SRP, soluble reactive phosphorus; SOC, soluble organic carbon; ICP, inductively coupled argon plasma emission spectrometer.

Al$_2$(SO$_4$)$_3$.14$H_2$O + 2$PO_4^{3-}$ + 2$AIPO_4$ + 3$SO_4^{2-}$ + 14$H_2$O
Fe$_2$(SO$_4$)$_3$.2$H_2$O + 2$PO_4^{3-}$ + 2$FePO_4$ + 3$SO_4^{2-}$ + 2$H_2$O
5$Ca(OH)_2$.3$H_2$PO$_4$.3$H^+$ + 3$Fe(F_2(SO_4)_3)$.9$H_2$O

(Ripley, 1974). Lime can be added as CaO or Ca(OH)$_2$. Similarly, ferric chloride or ferric sulfate appear to be equally effective. Sodium aluminate (Na$_2$Al$_2$O$_4$) has been used in the place of alum. Hsu (1976) indicated that the optimum pH for P removal with Al and Fe was dependent on the metal/P mole ratio. At metal/P ratios of two to five, the optimum pH range for P removal by Al was 5.5 to 8.0, whereas for Fe the optimum pH range was 4.7 to 7.1.

Poultry production provides an ideal setting for the use of chemical precipitants. At present, when broilers reach maturity and are removed from the houses, the litter, which is composed of a bedding material and manure, is collected and spread on adjacent pastures. This material has extremely high concentrations of water soluble P (>2000 mg P kg$^{-1}$). When the first heavy rainfall event occurs, P is transported with runoff water into nearby water bodies. If alum or slaked lime were applied to the litter prior to removal from the houses, the water soluble P could be converted to an insoluble mineral form via precipitation or adsorption, which would be less susceptible to leaching or runoff. The objective of this study was to determine if soluble P levels in poultry litter could be reduced using Al, Ca, and/or Fe amendments.

Prior to initiating field-scale studies, a laboratory incubation study was conducted to determine whether or not soluble P levels could be reduced in poultry litter and, if so, to ascertain which amendments would achieve this goal and critical levels of the various amendments.

**MATERIALS AND METHODS**

Twenty-six grams of fresh poultry litter (20 g dry weight equivalent) were weighed into glass bottles. The litter had been forced through a 2-mm sieve to break up large clumps and mixed in a portable cement mixer for 2 h to insure homogeneity. The bed of this litter was rice hulls. The litter had not been stacked in a portable cement mixer for 2 h to insure homogeneity. The litter was amended with Al, Ca, and Fe compounds to reduce P solubility. Materials tested included alum, sodium aluminate, quick lime, slaked lime, calcitic limestone, dolomitic limestone, gypsum, ferrous chloride, ferric chloride, ferric sulfate, and ferric sulfate. All amendments were reagent grade materials. After the amendments had been added, the mixtures were stirred with a spatula for 1 min. The Ca treatments were tested with and without CaF$_2$ additions as a secondary amendment in an attempt to precipitate fluorapatite. Calcium carbonate was added as a secondary amendment in cases where the primary amendment was believed to be an acid forming compound. There were 20 different chemical treatments tested, with five rates of each treatment (total number of treatments equaled 100 plus control) and three replications (Table 1). The lowest rate of the Fe and Al amendments was equal to the amount needed to achieve a 1:1 metal/P mole ratio, assuming the P content of the litter was 10 mg kg$^{-1}$. The lowest rate of the Ca amendments was based on a Ca/P ratio of 1.5:1. It should be noted that while the ratios were based on the assumption that the P content of litter was 10 mg P kg$^{-1}$, the actual P content was found to be 18.1 mg P kg$^{-1}$ (therefore, the lowest rate of Al and Fe was equivalent to 1:1.8 mole ratio).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Rate of primary amendment</th>
<th>Secondary</th>
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<tbody>
<tr>
<td>1. CaO</td>
<td>30, 60, 90, 120, 150</td>
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<tr>
<td>2. CaO + CaF$_2$</td>
<td>30, 60, 90, 120, 150</td>
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</tr>
<tr>
<td>3. Ca(OH)$_2$</td>
<td>40, 80, 120, 160, 200</td>
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</tr>
<tr>
<td>4. Ca(OH)$_2$ + CaF$_2$</td>
<td>40, 80, 120, 160, 200</td>
<td>5</td>
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<tr>
<td>5. CaCO$_3$</td>
<td>50, 100, 150, 200, 250</td>
<td>0</td>
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<tr>
<td>6. CaCO$_3$ + CaF$_2$</td>
<td>50, 100, 150, 200, 250</td>
<td>5</td>
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<tr>
<td>7. CaMg(CO$_3$)$_2$</td>
<td>100, 200, 300, 400, 500</td>
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<tr>
<td>8. CaMg(CO$_3$)$_2$ + CaF$_2$</td>
<td>100, 200, 300, 400, 500</td>
<td>5</td>
</tr>
<tr>
<td>9. CaSO$_4$.3$H_2$O</td>
<td>100, 200, 300, 400, 500</td>
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<tr>
<td>10. CaSO$_4$.2$H_2$O + CaF$_2$</td>
<td>100, 200, 300, 400, 500</td>
<td>5</td>
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<tr>
<td>11. Al$_2$(SO$_4$)$.18$H$_2$O</td>
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<tr>
<td>12. Al$_2$(SO$_4$).18$H_2$O + CaCO$_3$</td>
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<td>13. Na$_2$AlO$_4$</td>
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<td>14. Na$_2$AlO$_4$ + CaCO$_3$</td>
<td>25, 50, 75, 100, 125</td>
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<tr>
<td>15. Fe$_2$(SO$_4$).2$H_2$O</td>
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<td>16. FeCl$_3$</td>
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<td>17. FeCl$_3$.7$H_2$O</td>
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</tr>
<tr>
<td>18. FeCl$_3$.7$H_2$O + CaCO$_3$</td>
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<td>19. FeCl$_3$.4$H_2$O</td>
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<tr>
<td>20. FeCl$_3$.4$H_2$O + CaCO$_3$</td>
<td>60, 120, 180, 240, 300</td>
<td>100</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Calcium Amendments

Calcium oxide decreased the water soluble P levels in the litter from >2000 mg P kg\(^{-1}\) to <1 mg P kg\(^{-1}\) when an equivalent of 43 g Ca was added per one kg of litter (Fig. 1). It is not known whether this was due to precipitation or adsorption. Whatever the mechanism, the data suggest that soluble P runoff from fields receiving poultry litter could be decreased significantly if the litter were pretreated with CaO. The pH of the litter increased from 7.2 (control) to 8 at the higher rates of CaO (Table 2). A reduction in pH of the litter treated with CaO would be expected with time, due to equilibration with atmospheric CO\(_2\). This gradual reduction in pH may result in increased P solubility, since the solubility of Ca phosphates is extremely pH dependent. Even if the pH drops to 8, however, the equilibrium concentration of the most soluble Ca phosphate minerals, such as brushite (CaHPO\(_4\).2 H\(_2\)O), would be \(\approx 10^{-4}\) M or 3 mg P L\(^{-1}\) (Lindsay, 1979). This would still be roughly two orders of magnitude lower than soluble P levels determined for the litter used (200 mg P L\(^{-1}\)).

Recently, it has been determined that the majority of P runoff from land application of poultry manure occurs during the first runoff event (Edwards and Daniel, 1993). If soluble P levels could be decreased for at least a few weeks following land application, then there would be time for precipitation and adsorption by soils to occur, as well as uptake by plants and microorganisms. Therefore, if the solubility of P was lowered for only a short period of time, it would be beneficial from both an environmental and an agronomic viewpoint.

Calcium hydroxide decreased P solubility in poultry litter in the same manner as CaO (Fig. 1). Since Ca(OH)\(_2\) is less caustic, this treatment would be preferable to CaO, which can cause severe burns upon skin contact.

Calcitic and dolomitic limestone on P solubility in poultry litter had very little effect on SRP concentrations (data not shown). There are several possible reasons why these amendments did not work. One possibility is that the experiment was not carried out for a sufficient period of time. Normally, it takes months for limestone to completely react and neutralize soil acidity. Our incubation period was 1 wk, which may have been an insufficient time period for solubilization and precipitation reactions. Phosphorus adsorption by calcite should have occurred, since this is an extremely fast reaction. Kuo and Loise (1972) found that 80% of the phosphate sorption from inorganic P solutions by CaCO\(_3\) occurred within the first 10 s.

The pH of the unamended litter was initially 8.2, which decreased to 7.2 after 1 wk. Both calcite and dolomite are relatively insoluble at this pH, which may have led to inadequate amounts of Ca\(^{2+}\) in solution to precipitate P. Even if the Ca\(^{2+}\) concentrations in solution were low, however, P adsorption onto the calcite surface should have removed P from solution, as shown in previous research (Amer et al., 1985; Brown, 1980; Griffin and Jurinak, 1974; Stumm and Leckie, 1971). Phosphorus accumulation on calcite surfaces was described by Stumm and Leckie (1971) as a three-step process; (i) chemisorption of phosphate onto the surface causing the formation of amorphous Ca phosphate nuclei, (ii) a slow transformation of these nuclei into crystalline apatite, and (iii) crystal growth of apatite. In our study this process may have been inhibited by the high SOC levels in these treatments. High soluble C levels were measured in the extracts of samples that had relatively high pHS (Fig. 2). Innseek and Silvertoot (1988) showed that apatite precipitation was inhibited by the presence of soluble organic compounds, such as fulvic and humic acids. Magnesium and pyrophosphate, both of which are present in poultry litter, also inhibit this reaction (Amer and Mostafa, 1981; Amer et al., 1985; El-Zahaby and Chien, 1982).

Gypsum (CaSO\(_4\).2 H\(_2\)O) decreased SRP from >2000 mg P kg\(^{-1}\) to 700 mg P kg\(^{-1}\) at the 100 g kg\(^{-1}\) rate (Fig. 1). It should be noted that the lowest rate of gypsum used in this study was high enough to exceed the solubility product of gypsum (2.4 g L\(^{-1}\)). This helps to explain why in-

![Fig. 1. Effect of Ca amendments to poultry litter on water soluble reactive P.](image-url)
creased at the highest alum rates. This was believed to be due to the acidity created by the alum, which may have caused: (i) dissolution of inorganic Ca phosphates, (ii) acid hydrolysis of organic P, or (iii) dissolution of Al(OH)₃, which would result in P release if adsorption had been the primary mechanism of removal. The pH of the alum treated litter dropped to 3.5 at the highest rate (Table 2). Calcium phosphate minerals are highly soluble at this pH and could release enough P to achieve the P concentrations noted at the higher rates (Lindsay, 1979). Dicalcium phosphate is added to poultry feed to help insure proper bone development, since most of the P in soybean [Glycine max (L.) Merr.] and corn (Zea Mays L.) is phytate P, which is unavailable to chickens since they lack the phytase enzyme.

When CaCO₃ was added with the alum to buffer the pH, virtually 100% of the soluble P was removed from solution (Fig. 3). Hsu (1976) indicated that the optimum pH range for P removal by Al was 5.5 to 8.0, as stated earlier. Cooke et al. (1986) stated that alum removes phosphate from solutions by two different mechanisms, depending on the pH. Under acidic conditions (pH < 6) they indicated that AlPO₄ forms, whereas at pH 6 to 8, an Al(OH)₃ floc forms, which removes P from solution by sorption of inorganic phosphate and entrapment of organic particles containing P.

Other positive aspects anticipated with this practice would be a decrease in SOC levels in runoff water from litter-amended fields. Soluble organic C levels were relatively low under acidic conditions, whereas they tended to be high in the controls and in treatments that increased the pH of the litter (Fig. 2). Decreases in SOC concentrations and associated reductions in biological O₂ demand of wastewaters are one of the primary functions of flocculants used in wastewater treatment (Ulmgren, 1975). Decreases in SOC runoff should also improve water quality in lakes and rivers receiving runoff from pastures amended with poultry litter treated with acid forming products by decreasing O₂ demand. Addition of metal flocculants also decreased the solubility of Cu and Zn, which occur in high concentrations in poultry litter (Edwards and Daniel, 1992). Minimum solubility of both of these metals occurred at approximately pH 6 (data not shown).

Sodium aluminate decreased SRP levels to around 600 mg P kg⁻¹ at the lowest rate (Fig. 3). Increasing rates of Na aluminate did not decrease water soluble P, which was probably due to elevated pH at the higher rates. As mentioned earlier, the optimum pH range for P removal using Al is 5.5 to 8.0 (Hsu, 1976). Calcitic limestone as an additive to the Na aluminate treatment did not decrease soluble P (data not shown).

Additions of ferric Fe as Fe₂(SO₄)₃·2 H₂O or FeCl₃ greatly decreased P solubility at the lower rates, but increased the solubility at the higher rates (Fig. 4). Increases in SRP at the higher rates may have been due to: (i) dissolution of Ca phosphates, (ii) acid hydrolysis of organic P, and/or (iii) a decrease in adsorption of P by Fe compounds due to dissolution of Fe oxides and hydroxides at low pH. The pH of these two treatments approached 2 at the higher rates (Table 2). These values are well below the optimum pH range (4.7 to 7.1) for P removal by Fe reported by Hsu (1976). Therefore, removal using these compounds would
Additions of calcitic limestone in conjunction with ferrous chloride greatly decreased P solubility (Fig. 4). Water soluble P levels running off agricultural lands receiving poultry litter should help improve the water quality of adjacent lakes and rivers. It should be noted that alum and lime are relatively inexpensive and readily available. Calcium compounds, such as CaO or Ca(OH)₂, cost approximately $55 per megagram. Results from this study indicate that 50 kg of Ca(OH)₂ per megagram of litter may be adequate to immobilize most of the litter P. Since there are 20 megagrams of litter produced per house per growout (each house contains 15 000 to 20 000 birds), 907 mg of Ca(OH)₂ (slaked lime) is needed per house per growout. Assuming five growouts per year, the annual cost of slaked lime for one house would be $275. Gross incomes per house normally exceed $25 000 per year. Therefore, the cost of slaked lime needed for P immobilization would be ≈1% of the gross income, which should be economically feasible. Before a valid economic analysis of this process can be made, however, on-farm experiments need to be conducted to determine if treatment levels found in this study are adequate.

Although alum and ferrous sulfate are more expensive than Ca(OH)₂, the benefits of using these compounds should far exceed that of the Ca compounds. Lowering the pH of the litter will decrease NH₃ volatilization. High levels of NH₃ in poultry houses increase the incidence of ascites in poultry (water belly) and other respiratory related maladies, such as New Castle Disease (Anderson et al., 1964) and airsacculitus (Ehrlich, 1963). Since the amount of NH₃ volatilization is a function of the ratio of NH₃/NH₄ in the litter, which is controlled by pH, reducing the pH of the litter to ≈6.0 will cause N losses via this mechanism to cease. This should result in increased weight gains in the birds, as well as decreased incidence of respiratory problems.

Currently, the number one complaint received by federal and state regulatory agencies concerning poultry production concerns odors arising from land application of litter. Ammonia is one of the primary agents responsible for the odor. Wolf et al. (1988) estimated that 37% of the N is lost from litter during the first 11 d of application. If these losses were combined with those that occur in the houses, the total loss by volatilization would probably exceed 50% of the total N. Therefore, volatilization losses not only result in air pollution, but in losses of valuable fertilizer N. Decreasing NH₃ volatilization will result in higher N/P ratios in poultry litter. Currently, the N/P ratio in litter is often as low as 2, whereas the N/P ratio in the feed is near 8. The difference is mainly due to N loss via volatilization. Since application rates of litter are based on the N requirement of the crop, less litter could be applied per acre if the N content were higher.

**CONCLUSIONS**

The results of this study showed that a reduction in soluble P levels in poultry litter can be achieved using Al, Ca, and/or Fe amendments. Although P precipitation using chemical amendments has been used for >30 yr for wastewater treatment, there have been no reports in the literature of using this technology on animal manures. More research is needed in this area to determine: (i) if these results can be verified by field studies, (ii) if the P minerals formed by this process are stable in various geochemical environments, (iii) if this is an economically feasible practice, and (iv) if there are any other beneficial or detrimental side effects from this practice.
REFERENCES


