ACID MINE DRAINAGE TREATMENT RESIDUALS TO REDUCE PHOSPHORUS IN POULTRY LITTER[1]

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Abstract: Confined poultry production results in large quantities of phosphorus (P)-containing manure. The repeated application of manure to soils based on the nitrogen content of this material results in soil P buildup; a process that has been linked to eutrophication of surface waters. Active treatment of acid mine drainage produces an iron-based waste product, acid mine drainage treatment residuals (AMD-TR) that are known to bind inorganic and organic P. Our overall goal was to evaluate the feasibility of using AMD-TRs to reduce plant available P in poultry litter. The objective was to quantify the reduction and the variability of reduction in plant available P in poultry litter when AMD-TRs were incorporated. Inorganic P isotherms were constructed using six $Ca(OH)_2$-based AMD-TRs collected from northern West Virginia. Two of these were used in a wetting and drying incubation experiment with five poultry litters. Litter extractable P decreased by 190 to 680 mg P for every % (w/w) increase in AMD-TR, but was dependent on AMD-TR source and litter type. In a separate experiment, application of 20% AMD-TR to litter reduced extractable P by a factor of three, with a first order decay constant of 0.056 $(\% \text{ AMD-TR})^{-1}$. The potential for AMD-TRs to adsorb P from animal manures could convert what is now a liability (AMD-TR disposal) into an opportunity (P-management technology).

Additional Key Words: sorption, P removal, beneficial use

Introduction

Phosphorus from non-point source discharges is a major contributor to water quality degradation (Haustein et al., 2000). Phosphorus pollution has been linked to a wide array of problems including eutrophication, fish kills, loss of sea grass, and "dead zones" (Carpenter et al., 1998). In 1987, EPA set a maximum contamination level of 0.05 mg L^{-1} phosphorus in streams where it enters a lake or reservoir and 0.1 mg L^{-1} in streams that do not directly discharge into a lake or reservoir (USEPA, 1987).

Animal manure is an important soil amendment for agricultural soils because it has lime value, contains organic matter, and plant essential macro- and micro-nutrients (Haering and Evanylo, 2005). However, relative to plant needs, animal manures are enriched in phosphorus (P) such that repeated manure applications to meet fertilizer nitrogen (N) needs leads to excess soil test phosphorus (STP), especially in watersheds with extensive confined animal feeding operations (CAFOs) and limited arable land. There is a positive correlation between STP and dissolved P in runoff (Pote et al., 1996).

To address this problem, there are three potential solutions. First, excess manure could be removed from the watershed to P-deficient fields in another watershed. Second, manures could be applied to fields to meet P needs and supplemental inorganic N applied to meet N needs. Third, plant available P in the manure could be reduced so that land application more closely matches target plant N and P needs. The first two potential solutions have not, to date, been economically feasible.

Iron and aluminum oxyhydroxides have the ability to adsorb P from soil solutions (Barrow et al., 1980). Stable inner sphere complexes are formed because of the high affinity that phosphate has for exchanging surface ligands (Geelhoed, et al. 1998). Metal oxides have been used in the past to reduce phosphorus loss from non-point sources (Haustein et al., 2000; Rhoton and Bigham, 2005). Drinking water treatment residuals (TR) have been used to reduce P bioavailability and P-runoff from fields (Codling et al. 2000; Ippolito et al., 1999), but availability and cost have limited their use.

AMD treatment technologies also produce Fe and Al oxides that have the ability to adsorb P (Sekhon, 2002, Sibrell et al., 2002). The potential for AMD –TR to adsorb P from animal manure, could convert what is now a liability (AMD-TR disposal costs) into an opportunity

(P-management technology). However, AMD-TRs are known to be variable in composition, structure and reactivity due to a variety of factors including influent water quality, treatment type and age (Skousen and Ziemkiewicz, 1996; Lenter et al., 2002). Thus, not all AMD-TRs may be suitable for manure treatment. Animal manures are also variable due to species, diet, storage type and age (Haering and Evanylo, 2005).

Our objective was to quantify the reduction and the variability of reduction in plant available P in poultry litter when AMD-TRs were incorporated. To accomplish this, six AMD-TRs of the same treatment type and six raw poultry litters from two species (chicken and turkey) were used. The large number of experimental units necessitated the use of a sequential rather than a factorial experimental approach.

Materials and Methods

Sample Descriptions and Characterization

AMD-TR slurries that had been precipitated with calcium hydroxide ($Ca(OH)_2$) were provided by the West Virginia Department of Environmental Protection. Samples were air-dried, ground to pass a 2mm sieve and stored in plastic pails at room temperature until use. Total carbon (C) and sulfur (S) were determined by dry combustion (LECO TruSpec CHNS Analyzer, LECO Corp., St. Joseph, MI) before (C_{init}) and after (C_{final}) treatment with 1 M nitric acid (HNO_3) to remove carbonates. pH was determined 1:1 (w/w) in distilled, deionized water. Total elemental analyses (Fe, Al, Mn, Ca, Mg, and P) were determined by ICP-OES (Optima DV2100, Perkin Elmer Corp, Norwalk, CT) following microwave-assisted (MARS 5, CEM Corp. Matthews, NC) HNO_3 digestion (EPA 3051).

Five raw poultry litter samples, three chicken (A, B, C) and two turkey (D, E) were provided by the West Virginia Department of Agriculture. Samples were air-dried, ground to pass a 2mm sieve and stored in plastic pails at room temperature until use. Mehlich I extractable Ca, Mg, K, and P, and pH were determined as described above. A sixth chicken litter sample (F) was obtained later and used in a separate experiment.

A P sorption isotherm was constructed using 0.5 g of each AMD-TR and increasing concentrations of inorganic P as KH_2PO_4 such that equilibrium P concentrations ranged from zero to approximately 500 mg P L^{-1} in triplicate. Sorption maxima from the mean of triplicate isotherms were determined and compared using Analysis of Variance (ANOVA) with AMD-TR

type as a categorical variable and means separated by Least Significant Difference (PROC GLM, SAS ver 9.2, SAS Inst. Cary, NC). The AMD-TRs with the largest and smallest P sorption maxima were used in the first incubation experiment.

Incubation Experiments

The first AMD-TR - Litter incubation study was conducted by mixing 50.0 g of each of the first five litter samples (A – E) with 0, 0.25, 0.5, 1.25 or 2.5 g of the two AMD-TRs with the largest P sorption capacity as determined above (C and E). Samples were wet with just enough distilled deionized water to mix thoroughly and allowed to air dry in a dark incubator (~30°C). Samples were typically dry in two to three days. Each week a subsample was removed for pH and Mehlich I extractable Ca, Mg, K, and P determination, as described above. The remaining sample was rewet and the cycle repeated for a total of four weeks. Data were analyzed using PROC GLM (SAS ver 9.2, SAS Inst. Cary, NC) with AMD-TR type (n=2) and Litter type (n=5) as categorical variables and week (n=4) and added AMD-TR (%) (n=5) as regression variables. The initial statistical model was

Mehlich I P = AMD-TR + Litter + AMD-TR type x Litter type   **(1)**

+ AMD-TR (%) + week

The same procedure was repeated with one of the AMD-TR samples and a new litter sample (F) except that the mass of AMD-TR added was increased to 0, 0.5, 1, 2, 4, 5 and 10 g and subsamples were collected each week for three weeks. Data were fit using the SAS NLIN procedure (ver. 9.2 SAS Inst., Cary, NC).

All experiments except for the sorption isotherms were conducted in duplicate with duplicate subsamples. Although several elements were determined, only P is discussed in this paper. For all statistical analyses the significance level (α) was 0.05

Results

All AMD-TRs were basic in pH and contained between 1.1 and 12% Fe and between 2.2 and 6.2% Al (Table 1). The high pH and difference between $C_{initial}$ and C_{final} suggests the presence of calcium carbonate, a product of unreacted lime. The AMD-TRs contained small concentrations of native P (<110 mg kg^{-1}). The pH of all litter samples was between 6.5 and 8.4 (Table 2).

Turkey litters had larger P concentrations than did the chicken litters ($p<0.01$).   All litters samoles contained large K concentrations.

Table 1. Mean (n=2) pH, and total C, S, Fe, Al, Mn, Ca, Mg, and P for six $Ca(OH)_2$ precipitated acid mine drainage treatment residuals (AMD-TRs). $C_{initial}$ and C_{final} refers to before and after acid treatment to remove unreacted lime.

AMD-TR	pH	$C_{initial}$	C_{final}	S	Fe	Al	Mn	Ca	Mg	P
		---------------------------------- % ------------------------------------								mg kg^{-1}
A	8.0	1.4	0.54	1.3	13	4.4	2.4	5.0	2.5	78
B	8.3	2.4	0.85	1.5	12	5.4	0.4	8.2	2.9	110
C	9.3	2.4	0.41	3.2	10	3.4	0.3	19	1.0	44
D	9.2	3.7	0.43	2.3	1.8	2.2	3.2	12	2.3	68
E	8.4	3.5	0.55	1.5	1.8	5.8	0.9	14	3.3	86
F	8.2	3.1	1.1	0.90	1.1	6.2	2.5	2.0	2.6	110

Table 2. Mean (n=2) pH and Mehlich I extractable Ca, Mg, K, and P for six poultry litter samples.

Incubation	Litter	Type	pH	Ca	Mg	K	P
				----------------------- mg kg^{-1} --------------------			
1	A	Chicken	7.0	7300	3490	16900	8980
1	B	Chicken	8.4	6550	3270	14800	7900
1	C	Chicken	7.3	3820	3530	17000	6240
1	D	Turkey	6.5	5130	3170	16500	11000
1	E	Turkey	7.2	5300	3110	17600	10900
2	F	Chicken	6.9	5760	2870	27300	6900

AMD-TR-C had the largest P sorption maxima of approximately 70 g P kg^{-1} sludge, and AMD-TR-E had the smallest at 17 g P kg^{-1} sludge (Fig. 1).   All other samples had P sorption maxima of between 19 and 22 g kg^{-1} (data not shown).   AMD-TR-C had the highest Ca content (Table 1) which could indicate that unreacted lime or gypsum ($CaSO_4$) was the sorbent (Callahan et al., 2002) or that Ca-phosphates had precipitated.   There was no correlation between Fe, Al, or (Fe + Al) concentrations and P sorption capacity.   This may indicate the influence of oxide

morphology on P sorption (Torrent et al., 1990) which was not determined. The two AMD-TR samples with the largest (AMD-TR-C) and smallest (AMD-TR-E) P sorption capacities were used in the first litter incubation study.
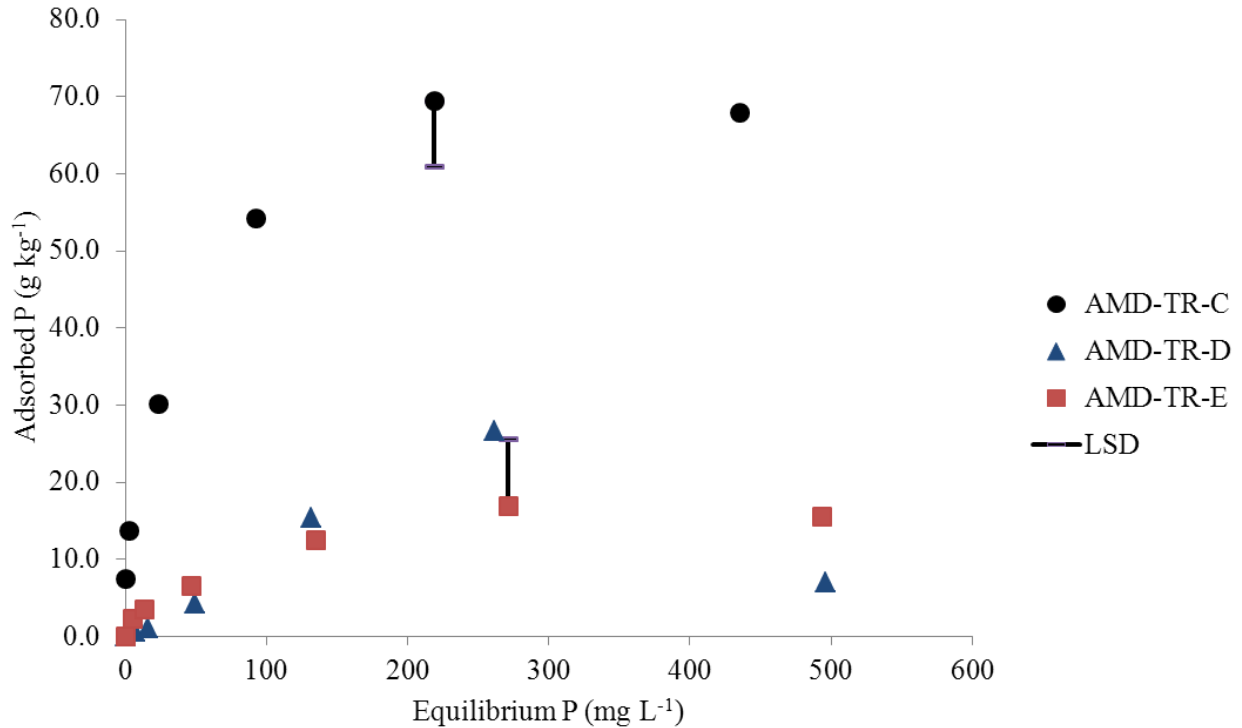

Figure 1. Mean (n=3) phosphorus sorption isotherms for three AMD-TRs. Isotherms for AMD-TR samples A, B and F were similar to sample D except with lower sorption maxima (data not shown). Error bars indicate LSDα=0.05 = 8.6 for P sorption maxima.

In the first incubation experiment, the statistical model (Eq. 1) was significant (p < 0.0001) and $R^2 = 0.913$. The effect of week was not significant (p = 0.1298) and so data were pooled and a simpler statistical model was analyzed individually by AMD-TR and Litter.

Mehlich I P = AMD-TR (%) **(2)**

Over the range of added AMD-TR phosphorus removal was linear, as determined by inspection of residuals. Removal capacities were between 190 and 680 mg P (% AMD-TR)$^{-1}$ depending on the litter sample (Table 3). Phosphorus removal with AMD-TR-C was greater than or equal to that of AMD-TR-E, except for Litter E, although this difference was not statistically different.

414

AMD-TR-C contained more Fe than did AMD-TR-E (Table 1) and so would be expected to adsorb more P.

Table 3. Mehlich I extractable P reductions for five poultry litters by two AMD-TRs as determined by Eq. 2. Standard errors in parentheses (n=8).

Litter	-- AMD-TR --	
	AMD-TR E	AMD-TR C
	----------------------------mg P (% AMD-TR)$^{-1}$ ----------------------------	
A	430 (50)	440 (30)
B	190 (20)	240 (40)
C	280 (20)	400 (20)
D	260 (40)	680 (50)
E	440 (70)	340 (50)

Phosphorus removal as a function of added AMD-TR-C in the second incubation with Litter F was not linear (Fig. 2) and so was fit with a first order decay function. Although curvilinear, there was no evidence of P saturation. The first-order decay constant was 0.0562 (AMD-TR%)$^{-1}$.

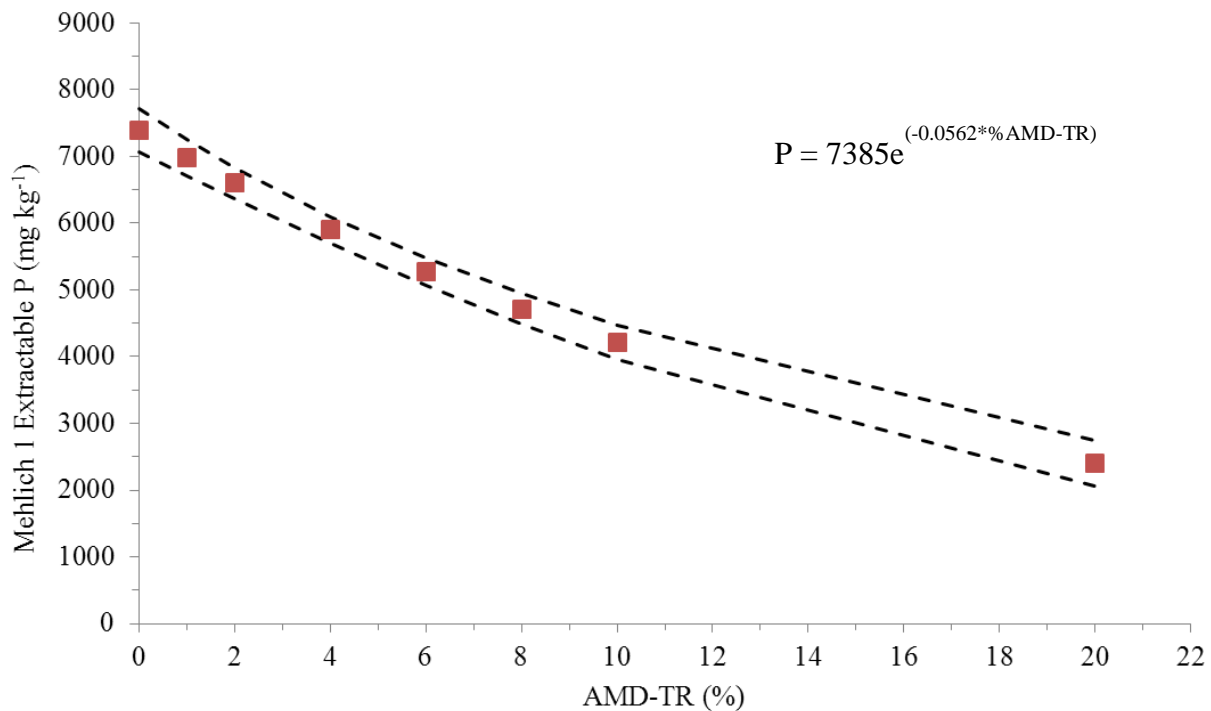

$$P = 7385e^{(-0.0562*\%AMD\text{-}TR)}$$

Figure 2. Mehlich I extractable P in poultry litter F as a function of added AMD-TR C. Dashed lines above and below data points indicate 95% confidence intervals (n=6).

Based on the result in Fig. 2, the data from the first incubation were also fit to a first-order function (Table 4). Decay constants were variable by litter although AMD-TR C had consistently better than or equal P removal than did AMD-TR E, except for litter sample E (Table 4). Results from the first-order analyses (Table 4) were consistent with the simple linear regression results (Table 3) with a Pearson correlation coefficient or 0.73 and a rank correlation coefficient of 0.98. There was no correlation (<0.43) between either the linear or first-order P reductions and initial P concentration in the litter. Litter sample F had a P concentration similar to sample C, but the decay constant was larger in incubation 1 (0.082 %$^{-1}$) than in incubation 2 (0.057 %$^{-1}$); further evidence that P removal is not simply related to litter P concentration. Although there was no *a priori* reason to fit a first order model to the data, some type of curvilinear function is appropriate because the P sorption capacity of AMD-TR is finite. It simply could not be justified given the data from the first incubation. Note that the range of AMD-TR added in the second incubation was four times larger than in the first incubation.

Table 4. First-order decay constants for Mehlich 1 P reduction for five poultry litters by two AMD-TR samples. Standard errors in parentheses (n = 6).

Litter	AMD-TR	
	AMD-TR E	AMD-TR C
	(% AMD-TR)$^{-1}$	
A	0.052 (0.002)	0.052 (0.005)
B	0.024 (0.004)	0.032 (0.006)
C	0.051 (0.002)	0.082 (0.002)
D	0.028 (0.006)	0.071 (0.004)
E	0.049 (0.007)	0.038 (0.005)

Conclusion

Calcium-hydroxide neutralized AMD-TRs reduced plant available P concentrations in poultry litter, but the effect was dependent on the AMD-TR and poultry litter. Differences in P removal varied by a factor of three whether determined by linear reductions (Table 3) or first-order decay (Table 4). There was considerable variability (> 3X) in removal effectiveness depending on the AMD-TR and Litter combination. P removal was not related to Fe and Al content of the AMD-TR or the initial P content of the litter. The reason for this variability

deserves more attention. However, because Mehlich 1 extractable P concentrations did not change after the first week, a specific AMD-TR – litter combination could be quickly evaluated for P-removal effectiveness with a relatively simple experiment.

Mehlich I P concentrations could be reduced by a factor of three with the application of 20% (w/w) AMD-TR. Potentially, this could bring plant available N and P in poultry litter closer to actual crop needs, reduce soil P build up and the associated water quality problems. However, the results from this study should be considered a best-case scenario because complete mixing of the AMD-TR and litter could be obtained, a result unlikely to occur under field conditions.

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