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Effects of N and P Immobilizing Agents on Ammonia Emissions and Nutrient Contents of Broiler Litter

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Abstract

Development of cost-effective treatments for broiler litter has become critical as broiler production continues to grow and the land available for manure spreading becomes more limited. Ammonia volatilization and nutrient losses are major forms of environmental pollution associated with land application of animal manures as fertilizers. A bench top study was conducted in the laboratory to determine the effect of nutrient immobilizing agents on ammonia emissions from broiler litter. The immobilizing agents include biochar, zeolite and flue gas desulfurization (FGD) gypsum were mixed with broiler litter at 10 and 20% by weight (w/w). Ammonia volatilization was measured over 7 days. Manure samples from the start and end of trials were analyzed for total N and were extracted with 1.0 M KCl and water with the extracts analyzed for ammonium, nitrate and water-soluble nutrients. Water-soluble N, P, Cu, Fe, Mn, and Zn levels in broiler litter were lower with FGD gypsum than with zeolite and biochar. Averaged across chemical additive rates, ammonia emissions from broiler litter were reduced by 68, 40 and 21% with the additions of zeolite, biochar and FGD gypsum, respectively. Ammonia emissions were not different between broiler litter treatment rates for FGD gypsum or biochar, however, the effect of zeolite on reducing ammonia emissions was much greater at 20% than 10%. Although addition of all agents to broiler litter reduced ammonia emissions, the abundant availability and lower cost of FGD gypsum and its potential for reducing P and heavy metal losses make FGD gypsum a better amendment for broiler litter than zeolite or biochar.

INTRODUCTION

Agricultural producers are under increasing pressure to reduce or eliminate adverse environmental impacts of management practices. Although most environmental concerns related to animal agriculture during the past two decades have focused on water quality, air quality is an important concern, too. Nitrogen losses from ammonia emissions have recently received significant attention. A conservative estimate is that 20-30% of the N contained in manure is volatilized during collection and application. This represents 715,000 tons of N released into the atmosphere annually with an agronomic value of nearly $300 million [1]. Tubail et al. (2008) reported that tremendous amounts of energy are required to replace this lost N by fixing atmospheric N in fertilizers, thereby reducing agricultural efficiency. The production, use, and disposal of large quantities of broiler litter. Ammonia volatilization from intensive livestock operation not only reduces fertilizer nitrogen value when manure is applied to agricultural land, but also contributes to environmental pollution which can endanger poultry and human health. Ammonia is generally formed when nitrogenous waste products in poultry manure are broken down by exogenous enzymes produced by microorganisms [2]. Ammonia is released directly from broiler production houses, during storage of litter, and after application of litter to soil [3]. Moore et al. [4] reported that emissions averaged 37.5 g NH_3 per bird from broiler houses during production, 0.172 kg NH_3 Mg^{-1} litter during a 16-day litter storage period, and 34 kg N ha^{-1} (15% of total N applied) after broiler litter was broadcast onto pastures. Many factors such as ambient temperature, ventilation rate, and pH can influence ammonia volatilization [5-7]. Miles et al. [8] reported that maximum NH_3 emission was up to 7 times greater at 40.6°C vs. 18.3°C. Although NH_3 loss is reduced at pH < 7, the pH of broiler litter is normally > 7 unless acidifying agents have been applied [2].

Georgia, Arkansas, Alabama, North Carolina and Mississippi are top major producers of commercial broilers in the U.S., and together deliver 78% of U.S. broiler production [9,10]. The broiler industry in Mississippi generates approximately 1 million Mg (1.2 million tons) of broiler litter yr^{-1} [11]. Applications of broiler litter to the surface of agricultural soils may increase N losses due to NH_3 volatilization, may increase the risk of eutrophication of adjacent surface waters due to increased phosphorus in runoff, and may increase levels of heavy metals such as copper (Cu) and zinc (Zn) in runoff [12-14]. In order to ensure in-house respiratory safety (for broilers and production workers) and to ensure the production of a stable, low-cost and high quality nitrogen fertilizer in the form of litter, nitrogen volatilization should be minimized. Downstream risks of eutrophication of surface waters from P and heavy metal accumulation in runoff also need to be reduced. Effective technologies that reduce ammonia loss during animal housing, manure storage and land application while minimizing adverse environmental impacts would have positive economic and environmental benefits. Manure treatment technologies to minimize air pollution associated with the production and use of broiler litter are needed, particularly in southern states where broiler production is concentrated and higher ambient temperatures favor higher emissions.

Several studies have sought to identify practices effective for reducing NH_3 emissions from broiler litter. One common strategy is the addition of amendments, which must be commercially available and reasonably priced. Dry acids, such as alum, are currently used to limit ureolytic bacterial growth, thus suppressing ammonia volatilization. Recent data suggest that alum is an efficient litter amendment, but safety of application, aluminum toxicity, and cost of application remain long-term concerns for the industry. Steiner et al. [15] reported that emissions of NH_3 were reduced by up to 64% when poultry litter was mixed with 20% biochar and noted that because biochar acts as an absorber of ammonia and water-soluble ammonium (NH_4) it might be an ideal agent for reducing ammonia emissions. Zeolite, a cation-exchange medium, is another agent that has high affinity for ammonium ions has been widely used to reduce ammonia in water [16]. Zeolites and biochars are produced by mining and by pyrolysis of organic materials, respectively, and are generally too costly for use as manure amendments on a wide scale. Flue gas desulfurization (FGD) gypsum is a unique a coal power plant by-product resulting from scrubbing coal smoke to prevent SO_2 release into the atmosphere. The use of flue gas desulfurization (FGD) gypsum offers the poultry industry an alternative litter amendment for reducing ammonia volatilization. There are a number of potential benefits of applying FGD gypsum include supplying essential plant nutrients calcium (Ca) and sulfur (S) for crop production and the promotion of clay flocculation and aggregation of the soil, reduction of surface crusting which leads to increased water infiltration. Millions of tons of high quality FGD gypsum are produced each year in the United States as a result of scrubbing sulfur dioxide from flue gasses during coal combustion. The primary cost of FGD gypsum utilization is shipping and handling which may deliver the by-product to the end users free of charge. The effect of FGD gypsum as a P immobilizing agent has been widely reported. Favaretto et al. [12] reported that application of gypsum at 5000 kg ha^{-1} reduced losses of dissolved reactive P, total P, and total N by 85, 60, and 59%, respectively. The potential of FGD gypsum on reducing ammonia volatilization has also been reported. Chowdhury et al. [17] reported that FGD-gypsum is expected to alter the osmotic and matric potential of broiler litter, which would decrease the activity of litter microorganisms responsible for urea N degradation and thus reduce ammonia volatilization; however, limited information is available on the effects of gypsum on ammonia emissions. Koenig et al. [18] reported that addition of gypsum to poultry manure significantly reduced ammonia emissions during composting poultry manure with wood chips. The availability of vast quantities of low cost FGD gypsum, and the potential of reducing N and P losses, makes this by-product a good amendment candidate for broiler litter. The efficacy of FGD gypsum as amendment to broiler litter relative to zeolite and biochar has not been tested and little information is available on the proper mixing ratios of the agents with organic materials and the amounts of N saved as a result. We hypothesized that mixing FGD gypsum with broiler litter prior to use would reduce ammonia emissions, losses of N, P and heavy metals. The objective of the present study was to quantify the effects of FGD gypsum relative to zeolite and biochar, at different amendment ratios with broiler litter, on NH_3 emissions, water-soluble P, and heavy metals.

MATERIALS AND METHODS

Experimental design

An initial laboratory-scale experiment was conducted to evaluate the effect of nutrient immobilizing agents FGD gypsum, zeolite and biochar on ammonia emissions from broiler litter. Seven treatments with three replications were tested. Treatments included nonamended broiler litter (control), broiler litter plus FGD gypsum, broiler litter plus zeolite, and broiler litter plus biochar. Each amendment was added to broiler litter at two rates, 10 and 20% (w/w). Treatments were arranged in a randomized complete block design that involved air supply manifolds (blocks) for collection of NH_3 emissions. Each experimental unit contained 100 g of broiler litter plus FGD gypsum, zeolite, or biochar. Ammonia emissions were measured from each unit by entrapment in boric acid solution daily for eight days. At the termination of the experiment, all replicates of litter were weighed and subsamples (50g) were taken for chemical analyses.

Chemical analyses of broiler litter, FGD gypsum, zeolite, and biochar

Flue gas desulfurization gypsum was received from power plants in Georgia. Zeolite was received from ZEO INC, McKinney, Texas. Biochar was received from the USDA, ARS, Southern Regional Research Center, and New Orleans, Louisiana. Rice hull-based broiler litter used in the experiment was obtained from a commercial farm in Mississippi. At the start of the experiment, the moisture content of the litter was 26.5%±0.0043 (n=3) as determined by weighing samples before and after drying in an oven at 110°C for 24 hr. Litter pH was determined from a suspension of one part litter mixed into five parts de-ionized water and measured using a pH meter with glass electrode.

Total N and C contents were determined using an automated dry combustion method with a Thermo Quest C/N analyzer (CE Elantec, Inc., Lakewood, NJ). Separate subsamples of the litter were extracted with either 200 mL of deionized (DI) water or 200 mL of 2 *M* KCl for 2 h, centrifuged at 6000 rpm for 5 min, filtered (0.45-µm filter), and aliquots analyzed for water-soluble C, organic C (OC), inorganic C (IC), and N using a Shimadzu TOC-VCPH combustion oxidation TOC analyzer. Ammonium (NH_4^+) and NO_3^- concentrations were determined using a Lachat QC 8000 flow injection analyzer (Lachat, Loveland, CO).

Total P, K, Ca, Mg, Cu, and Zn contents were determined using a dry-ashing procedure [19]. Approximately 1 g of dry litter, finely ground to pass a 1 mm sieve, ashed in a muffle furnace (Model 30400, Thermolyne Corp., Dubuque, IA) at 500°C for 4 h. The ash was resuspended in 1.0 mL of 6 *M* HCl for 1 h, added to 50 mL of a double-acid solution (0.0125 *M* H_2SO_4 and 0.05 *M* HCl) and allowed to stand for 1 hour, and then filtered using #2W filter paper [19]. The filtrate was analyzed for P, K, Ca, Mg, Cu, and Zn contents using an inductively coupled plasma spectrometer (ICP, Thermo Jarrel-Ash model 1000, Franklin, MA). Water-soluble P, K, Ca, Mg, Cu, and Zn contents of litter were determined from samples mixed (1:20) in DI water, shaken for 1 h, centrifuged at 3500 rpm for 10 min, and filtered through Whatman filter paper #2 (Source info for brand name Whatman) followed by ICP analysis of the filtrates. Chemical properties of broiler litter, FGD gypsum, zeolite, and biochar at the start of the experiment are listed in Table 1.

Experimental units and NH_3 measurement

Ammonia emissions were measured daily from each unit by entrapment in boric acid solution. A chamber acid trap (CAT) system described by Miles et al. [20] was used for determining NH_3emissions from broiler litter treatments. The CAT system offers precision control of air flow rate through sample chambers as well as straightforward, precise determination of the amount of N volatilized. Forty-eight sealed 1-L chambers accommodate litter samples (Figure 1), which are weighed and have a uniform surface area (94 cm^2). Four manifolds supply water-scrubbed air to circulate into each sealed container at approximately 110 mL/min. Exhaust air from each container flows through a series of 2 H_3BO_3 traps (50-mL Erlenmeyer flasks), each containing 30 mL of H_3BO_3 indicator solution. The purpose of the duplicate traps is to ensure that no NH_3 is lost should the first trap become saturated before titration. The H_3BO_3 is used to capture NH_3 emitted from the sample. The contents from the 2 flasks are combined and titrated with 0.1*M* HCl. The titration endpoint is based on color change [21] in which the color of the solution changed from blue green to light pink. Trap flasks were rinsed with DI water after each day's use and 30 mL of fresh 1 *M* H_3BO_3 added and the traps reconnected to the chambers for the next collection. The samples were incubated at 22°C±3°. The solutions from the two flasks was combined into a single sample and titrated with. The NH_3 trapped in the solution was quantified and reported as mg N recovered. The N loss from each litter sample was calculated according to the following formula.

$$\text{mg of N} = (\text{mL of HCl}) \times (\text{HCl molarity}) \times MW_N$$

The percent loss of N, as ammonia, was calculated by dividing the total cumulative amount of N in the trap solutions by the total initial N in each treatment using the formula below [22]

$$NH_3\text{-N lost (\% of initial)} = [(\text{HCl (ml)} \times 9.29 \text{ mg } NH_3\text{-N ml}^{-1}) / \text{mg initial N}] \times 100$$

where 9.29 mg NH_3-N ml^{-1} is an empirically determined titration factor. Cumulative N loss in the form of NH_3 for the litter treatments was calculated by summing the mg of N generated each day.

Table 1: Initial chemical properties of broiler litter and the immobilizing agents gypsum, zeolite and biochar used in the study (n=3).

Category	Chemical properties	Broiler litter	immobilizing agents		
			FGD	Zeolite	Biochar
Moisture (%)		34	-	-	-
pH		8.3	7.8	8.6	8.8
C fractions	Total C(%)	34.85	0.201	0.019	46.2
	Water-soluble C(mg/g)	51.9	0.048	0.09	28.36
	Water-soluble OC(mg/g)	46.1	0.024	0.087	17.42
N fractions	Total N (%)	2.95	0	0	0.17
	Water-soluble N(mg/g)	15.9	0.024	0.029	0.054
	NH4(mg/g)	5.69	0.006	0.001	0.013
	NO3(mg/g)	0.33	0.037	0.039	0.006
Total metal concentrations	P(g/kg)	11.1	0.107	0.072	37.9
	K(g/kg)	19.7	0.473	20.6	72.3
	Ca(g/kg)	18.3	152.7	5.73	55.2
	Mg(g/kg)	4.3	0.358	0.182	15.4
	Cu(mg/kg)	85.6	4.052	0.606	560
	Fe(mg/kg)	316	393.1	521.9	1928
	Mn(mg/kg)	357.2	8.505	101.9	1170
	Zn(mg/kg)	331	14.3	0.710	958

Data analysis

The experiment was a randomized complete block design with 11 treatments replicated three times. Data were subjected to analysis of variance (ANOVA) using the PROC GLM statement of the SAS statistics program [23]. When ANOVA generated a significant F value for treatment ($P<0.05$), means were compared by the LSD test.

RESULTS AND DISCUSSION

pH and ammonia emission

Understanding how ammonia is formed is the key to understanding how manure can be managed to minimize ammonia emissions. Nitrogen excreted in the form of urea (in mammals) or uric acid (in birds) in livestock and poultry wastes, respectively, occurs in manure in the forms of urea, ammonia, and organic nitrogen. The nitrogen is converted to either ammonium (NH_4^+) under acidic or neutral pH conditions or ammonia (NH_3) at higher pH levels. The effect of pH on the amount of NH_4+and NH_3 formed is crucial in determining the fate of manure nitrogen. At the end of the experiment, all amendment treatments reduced the pH of treated broiler litter compared to untreated control (Figure 2). This may partly explain some of the amendments' abilities to reduce ammonia volatilization during the incubation time. However, the pHs were similar when the amendment rate increased from 10 to 20% of the weight of broiler litter (w/w). The effect of zeolite in reducing broiler litter pH was much greater than that of the other two amendments (Figure 2).

Cumulative NH_3 emissions of all treatments for 7 days are shown in Figure 3. Ammonia volatilization from zeolite- and biochar-amended litter peaked during the first 2 days of the study, then tapered off and was almost nil by the end of the week, while ammonia emissions from control litter and FGD gypsum-amended litter increased steadily until day 6, then tapered off (Figure 3).

Addition of FGD gypsum at 10 and 20% decreased ammonia emissions compared to the controls (broiler litter only), by 19 and 24%, respectively (Figure2). Although the magnitude of ammonia emission at the 20% FGD gypsum application rate was greater than at the 10% application rate, the difference was not significant (Table 2 and Figure 3). In agreement with our results, Koenig et al. [18] reported that addition of gypsum to poultry manure at rates of 4% and 12%, when composting, significantly decreased evolution of ammonia. Generally Acidifying manure generally plays an important role in reducing ammonia volatilization; however, for FGD gypsum-amended litter, the reduced ammonia emissions were not the results of broiler litter acidification because the pH of gypsum-treated broiler litter was above 7 (Figure 2).). The moisture content of broiler litter was reduced by 5.6% and 9.7%, respectively, at 10% and 20% amendment rates with FGD gypsum. Reduced moisture content of manure by addition of gypsum may increase litter matric

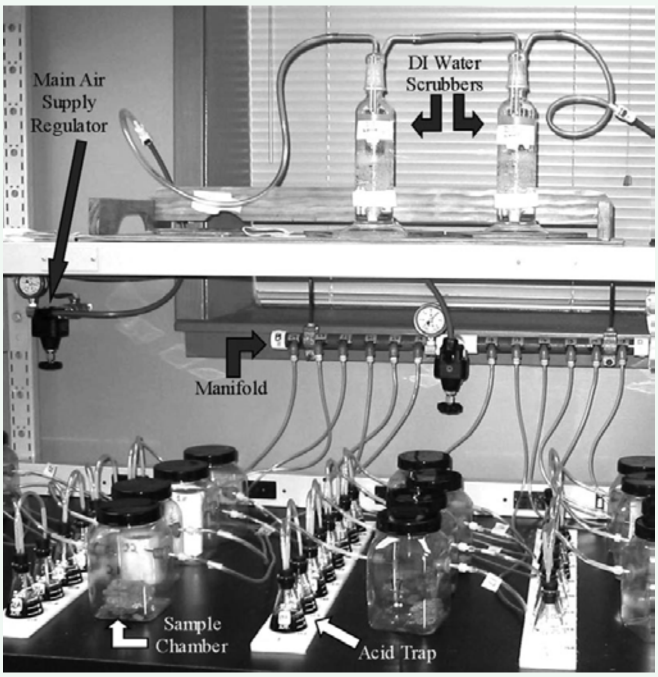

Figure 1 Partial front view, showing major components of chamber acid trap system was used for determining NH3 losses from litter treatments. DI = de-ionized water [20].

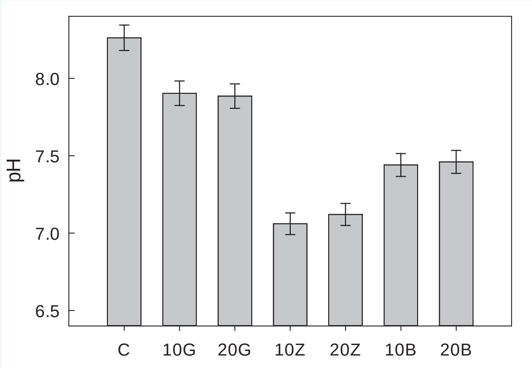

Figure 2 pH levels of different treatments at termination of the experiment. Each bar represents the mean value for 3 replicate samples. Treatment abbreviations are CK: Control; G: FGD gypsum; B: biochar; and Z: zeolite. 10, and 20 g of agent mixed per 100 g of broiler litter.

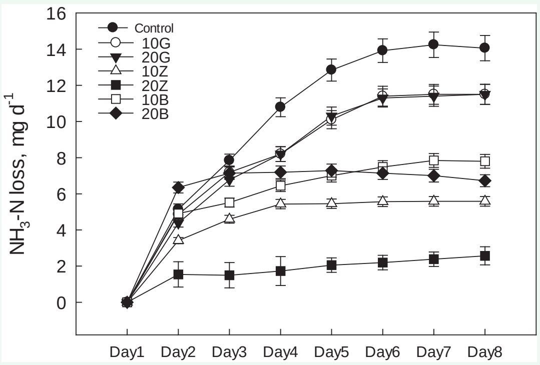

Figure 3 Cumulutive NH3 emissions from broiler litter in 7 days. Each bar represents the mean value for 3 replicate samples. Treatment abbreviations are CK: Control; G: FGD gypsum; B: biochar; and Z: zeolite. 10, and 20 = g of agent mixed per 100 g of broiler litter.

Table 2: Nitrogen fractions measured in samples of broiler litter from experimental treatments at termination of the experiment (n=3).

Treatments	Ammonia Emission	Water Extraction N	2 *M* KCl Extraction NH_4^+	NO_3^-
	----------------- mg ----------------		------------- mg l^{-1}------------	
CK	79 a	1544 a	3254 d	360 a
10G	64 b	1317 e	4153 c	393 a
20G	60 bc	1340 de	4652 a	391a
10Z	34 e	1390 bc	4345 b	370 a
20Z	13 f	1420 b	4156 c	372 a
10B	45 de	1372 cd	2653 e	364 a
20B	49 dc	1418 b	2454 f	333 a

Note: Means followed by different letters are significantly different at $P< 0.05$ according to analysis of variance and Fisher's protected LSD test. Treatment abbreviations are CK = Control, G = FGD gypsum, B = biochar, and Z = zeolite. The number 10 and 20 are gram of agent mixed per 100 g of broiler litter

potential which affects microbial activity. The mode of action of gypsum in reducing ammonia volatilization was suggested by Chowdhury et al. [17] who reported that FGD-gypsum is expected to alter the osmotic and matric potential of broiler litter, decreasing the activity of litter microorganisms responsible for urea N degradation and reducing ammonia volatilization. At the end of the present experiment litter amended with gypsum had the lowest water extractable N content which was 253.0 mg lower than the control (1340 vs. 1577 mg, respectively) (Table 2), while extractable NH_4+-N increased probably caused by NH_4^+ displacement with Ca [24]. Zeolite additions at 10 and 20% application rates also reduced ammonia emissions compared to the controls (broiler litter only). The 20% zeolite application rate substantially reduced ammonia emission when mixed with broiler litter and had the lowest level of NH_3 emission releasing only approximately 20% of the amount released from the controls during seven day, experiment (Table 2). The effect of zeolite on reducing ammonia emissions was generally proportional to the application rate. For example, addition of zeolite to broiler litter at the 20% rate resulted in reduction of ammonia emission by 80% compared to broiler litter only (Table 2 and Figure 3), while addition of zeolite to broiler litter at the 10% rate reduced ammonia emission by 47%.Reduced ammonia emissions in zeolite treatments were not the result of broiler litter acidification because the pH of zeolite-treated broiler litter was above 7 (Figure1). Zeolite is a cation-exchange medium with high affinity for ammonium (NH_4) ions[16,25,26], and our results confirm that zeolite treatments retained NH_4^+, therefore, NH_3 emissions were reduced significantly, particularly at the 20% rate. The mode of action of zeolite in reducing ammonia volatilization is most likely a reduction of broiler litter-derived ammonium (NH_4^+ -N) due to equilibrium between total ammoniacal N and exchangeable NH_4^+ -N which is held on inorganic site of broiler litter. Addition of zeolite to broiler litter increases the number of NH_4^+-N exchange sites, which bind more NH_4^+ -N decreasing the quantity of water-soluble NH_4^+-N and the quantity of equilibrated NH_3-N gas available for ammonia volatilization [27]. Zeolite results from our study are in agreement with the work by Lefcourt and Meisinger [27] who reported that zeolite additions at 2.5% and 6.25% into dairy slurry reduced NH_3 emissions by 22% and 47%, respectively, over a 4-d storage period. The amounts of ammonia (NH_3) released by the litter, from the lowest to the highest of the amendment treatments in the present study were zeolite < biochar <FGD gypsum <control (manure only).

Addition of biochar to litter significantly reduced ammonia emissions (P= 0.031) by approximately 30% as compared to broiler litter only (Figure 3).The effect of biochar in this study was independent of the application rate and no differences in ammonia emissions were observed between the 10% and 20% rates (Figure 3). Steiner et al. (2010) reported that application of biochar at the 20% rate reduced ammonia emissions up to 64% as compared to broiler litter only. Biochar is believed to absorb NH_4^+ ions predominantly by cation exchange, thus preventing ammonification and reducing NH_3 emissions [28,15] .

Macro- and Micro-nutrients

Gypsum treatments significantly increased total Ca but did not affect total P, Mg, K, Ca, Fe, Mn, and Zn. Only at the higher rate, addition of zeolite to litter increased total K by 17% as compared to the control. Biochar significantly increased levels of all nutrients as compared to the control and other amendments, due to high levels of these elements in biochar (Table 1), and the effect was greater at the higher application rate (Table 3). Addition of biochar at the 20% rate increased total P, Ca, Mg, K, Ca, Fe, Mn, and Zn contents by 26, 29, 26, 24, 31, 36, 26, and 22%, respectively, as compared to the 10% rate (Table 3).

Water-soluble nutrient concentrations were included in this study because nutrient losses from land-applied animal manure are related to water-soluble nutrient contents of the organic fertilizer [29]. Addition of gypsum to broiler litter greatly increased water-soluble Ca and Mg contents in broiler litter. Water-soluble Ca in the treatment with 20% gypsum reached 767 mg in comparison to 49 mg in the control. Zeolite and biochar did not affect Ca. Addition of zeolite at the 20% rate decreased water-soluble K which implied that zeolite may immobilize (adsorb) a portion of the K in litter by its cation-excahage capacity potential, similar to its effect on NH_4^+ adsorption. Biochar, which contains very high level of K (Table 1), increased K content of litter by 14% at the 10% rate and 25% at the 20% rate (Table 4). Biochar, which had a Mg concentration about three times higher than broiler litter (Table 1), did not increase water-soluble Mg content in amended litter (Table 4), but did increase total Mg levels, especially at the 20% rate (Table 3).

Gypsum significantly reduced the levels of water-soluble P and micronutrients in amended litter (Table 4). Averaged across application rates, the water-soluble P, Cu, Fe, Mn, and Zn in FGD

Table 3: Total nutrient levels measured in samples of broiler litter from experimental treatments at termination of the experiment (n=3).

Treatments	P	Ca	Mg	K	Cu	Fe	Mn	Zn
	------------------- g -------------------				------------------- mg -------------------			
CK	11.4c	19.9 c	4.3 b	20.3 c	90 c	274 d	357c	358 c
10G	11.3c	29.7 b	4.3 b	21.0 c	85 c	219 e	306 d	305 d
20G	11.7c	34.6 a	4.5 b	21.5 c	94 c	326 c	366 c	339 d
10Z	10.8 c	19.1 c	4.3 b	21.6 c	74 e	457 b	354 c	325 d
20Z	11.4 c	21.6 c	4.4 b	24.2 b	75 e	621 a	365 c	318 d
10B	14.4 b	22.2 c	5.6 b	26.7 b	133 b	425b	451 b	408 b
20B	19.4 a	31.1b	7.6 a	35.3 a	193 a	666 a	606 a	528 a

Note: Means followed by different letters are significantly different at *P*< 0.05 according to analysis of variance and Fisher's protected LSD test. Treatment abbreviations are CK = Control, G = FGD gypsum, B = biochar, and Z = zeolite. 5, 10, and 20 = g of agent mixed per 100 g of broiler litter

Table 4: Water-soluble nutrient levels measured in samples of broiler litter from experimental treatments at termination of the experiment (n=3).

Treatments	Ca	K	Mg	P	Cu	Fe	Mn	Zn
	------------------------------------- mg -------------------------------------							
CK	49 c	1654cd	42 c	140 a	5.9 a	4.5ab	1.5 a	5.7 a
10G	358 b	1700 c	150 b	52 d	4.4 b	2.5 c	1.1 c	3.8 d
20G	767 a	1615 d	185 a	48 d	3.3 c	1.8 c	1.3 c	2.9 e
10Z	50 c	1342 e	40 c	129 abc	4.9 b	5.0 ab	1.4 ab	4.9 bc
20Z	54 c	1104 f	43 c	124 c	4.5 b	5.7 a	1.3 ab	4.4 dc
10B	46 c	1928 b	37 c	137 ab	5.5 a	4.1 b	1.4 ab	5.3 ab
20B	40 c	2179 a	34 c	127 bc	5.6 a	3.9 b	1.2 bc	4.7 bc

Note: Means followed by different letters are significantly different at *P*< 0.05 according to analysis of variance and Fisher's protected LSD test. Treatment abbreviations are CK: Control; G: FGD gypsum; B: biochar; and Z: zeolite. 5, 10, and 20 = g of agent mixed per 100 g of broiler litter

gypsum-amended broiler litter decreased by 64%, 35%, 52%, 20%, and 41%, respectively, as compared to the control. Moore and Miller (1994) and Dou et al. (2002) [30,31] also reported that gypsum reduced water-soluble P levels in manure. The reduction is attributed to the conversion of readily de-sorbable soil P in solution to less soluble Ca-bound pools [32]. Addition of zeolite to broiler litter significantly reduced the water-soluble Cu and Zn in litter by 20 and 18%, respectively. Consistent with our results, Turan (2011) 33 reported that natural zeolite can remove considerable amounts of Cu and Zn from aqueous leachate of poultry litter. Park et al. (2013) [34] reported that biochar has the potential to reduce concentrations of bioavailable heavy metals such as Cd, Cu, and Pb; however, our results showed that biochar did not reduce water-soluble levels of P, Cu, Fe, Mn, or Zn in litter amended at the 10% rate, but did reduce water-soluble P, Mn, and Zn at the 20% rate (Table 4).

The present study evaluated the effects of three litter amendments on water-soluble and water-insoluble elements and compounds that, under conducive conditions, may be released or retained by poultry litter. Although other studies have examined individual effects of immobilizing agents on NH_3 emission, nutrient loss, or heavy metal availability, these effects had not been investigated together. Results of the present study indicate that the three agents studied here all have effects that are unique, that differ in magnitude, or that may even be contraindicated for application when reduction of some elements or compounds is the objective. Differences observed between litter amendments may be beneficial as they present amendment options for mitigating different environmental problems. For example, where NH_3 emissions or soluble-N losses are the major concerns, zeolite, alone or in combination with other amendments, might be a preferred choice for mixing with poultry litter. Where minimizing losses of water-soluble P, N or metal elements is the objective, gypsum might be the more desirable amendment. Overall, considering the wide range of potential problems that accrue from repeated land-applications of poultry litter, a mixture of 5% gypsum and 5% zeolite might be an effective choice to prevent losses of volatile, metallic, and water-soluble elements and compounds, providing lower accumulations of Ca and Mg than might occur with 10% gypsum alone. Use of these amendments alone or in combinations may help to mitigate or minimize specific environmental problems that could result from repeated land-applications of poultry litter.

In addition to effectiveness, the costs and availability of amendments are other factors that must also be considered in making decisions about which immobilizing agents or combinations should be used. If the cost is too high for a particular agent, it may be necessary to use a less effective agent in order to make control practices cost-effective. Results of the present study provide information useful in identifying the most appropriate agent or combination to optimize effectiveness and reduce costs for producers.

CONCLUSION

The findings of the present study showed that addition of zeolite to broiler litter substantially reduced NH_3 emissions and that the effect was generally proportional to the application rate. Adding biochar to litter significantly decreased NH_3 emissions and water-soluble N in the litter. Addition of biochar to broiler litter significantly increased C, P, Ca, Mg, K, Cu, Fe, Mn, and Zn in the litter due to high levels of these elements in the agent. Adding FGD gypsum to litter reduced ammonia emissions and significantly reduced water-soluble P and heavy metals in the litter. Although addition of all agents to broiler litter reduced ammonia emissions, the abundance of FGD gypsum its relatively low cost and its potential to reduce water-soluble P and heavy metals make FGD gypsum a more economical, effective and environmentally-friendly amendment for broiler litter than zeolite or biochar.

Additional future research on processes and mechanisms associated to these agents is necessary to better understandthe properties and to exploring further uses of zeolite, biochar and FGD gypsum in order to meet the new mitigation guidelines and strategies for best management practices.

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