RESEARCHREPORT

ENVIRONMENT

Title: Alternative calcium and phosphorus sources for reducing ammonia emission through manipulation of excreta pH - **NPB #00-043**

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I. Abstract:

Ammonia emission can be reduced through lowering manure pH. Although such a reduction can be achieved by adding acids in the pit, greater reductions in ammonia emissions can be expected when excreta pH is lowered through the diet as a substantial portion of ammonia is emitted from slats. Feeding acidogenic phosphorus sources such as phosphoric acid and monocalcium phosphate was effective in reducing urine pH with 1 pH unit and both, when fed with suitable calcium sources, resulted in lowered ammonia emission (30 and 16%, respectively). A major dilemma encountered in these experiments was the calcium source to use; calcium carbonate (limestone) increases urine pH, in contrast to calcium sulfate (gypsum) or calcium chloride. The latter two, however, may negatively affect gut and animal health, therefore increasing odors. In growth performance experiments they also led to poor animal performance. In conclusion, for reducing ammonia emission, phosphoric acid and monocalcium phosphate are preferred over dicalcium phosphate as phosphorus sources. Calcium chloride and calcium sulfate are calcium sources that can lower urine pH but as they negatively affect animal performance, limestone remains the preferred source of calcium.

II. Introduction:

Ammonia emission from swine facilities should be reduced to prevent water and air pollution (Apsimon and Kruse-Plass, 1991) and to reduce possible health problems with humans working with hogs or living in the vicinity of hog facilities (Schiffman, 1998). The major source of ammonia emission is urea excreted with urine. This urea is converted into ammonia and carbon dioxide by the urease present in feces (Stevens et al., 1989). Emission of ammonia from manure, however, is strongly dependent on pH; low pH traps ammonia in the manure in the form of ammonium salts. The pH of manure can be lowered through feeding acidogenic compounds, and in this study the efficacy of acidogenic calcium and phosphorus sources on ammonia emission was investigated.

III. Stated objective:

The pH (acidity) of pig excreta can be easily and economically managed through nutritional means. Reducing excreta pH is known to reduce ammonia emission; however, its impact on odor has not been characterized. The objectives of the research proposed are 1) to evaluate the impact of a practical and economical means to reduce urine pH on ammonia and odor emission, and 2) to provide guidelines for diet formulation that will reduce excreta pH to the level needed to minimize air pollution.

IV. Procedures:

General: The North Carolina State University Institutional Animal Care and Use Committee approved all experimental procedures, care, and handling of animals.

Experiment 1: Impact of acidogenic agents on urine pH. A total of eight crossbred finishing barrows (initial BW 67 kg) were used to test diets that contained monocalcium phosphate, phosphoric acid, calcium sulfate, and/or hydrochloric acid as acidogenic agents. The diets tested were as indicated in Table 1. Pigs were housed in individual pens and received water *ad libitum*. Feed was provided twice per day at the rate of 80 g per kg metabolic body weight ($BW^{.75}$). Urine samples were collected on Day 6 and 7 following a 5-day adaptation for determination of urine pH using a standard pH electrode.

Table 1. Composition (in percent) of diets as used in Experiment 1.

Items	**Control**	**Monocalcium phosphate**	**Phosphoric acid**	**Hydrochloric acid**
Ground corn	76.26	76.26	76.26	76.26
Soybean meal (CP 48%)	15.36	15.36	15.36	15.36
Poultry fat	3.98	3.98	3.98	3.98
Dicalcium phosphate	1.10	-	-	1.10
Monocalcium phosphate	**-**	**0.97**	**-**	**-**
Phosphoric acid	**-**	**-**	**0.81**	**-**
Calcium carbonate	0.85	-	-	-
Calcium sulfate	**-**	**1.75**	**2.50**	**1.39**
Hydrochloric acid	-	-	-	0.47
Salt/Vit-Min & filler	2.45	1.68	1.09	1.44
Diet pH	5.54	5.19	3.98	3.59

Experiment 2: Impact of acidogenic agents on ammonia and odor emissions. To evaluate the impact of diet composition on ammonia and odor emission, a total of five trials were conducted. In each trial the effect of one acidogenic diet on emission was compared with emissions observed on a control diet (Table 2). For this experiment, pigs were housed in environmental chambers of $7 \times 9 \times 8$ ft which contained a pig-pen (7×8 feet) that housed 10 pigs and which was positioned above a pit designed for pit-recharge. Manure was stored in this pit for a one-week period, after which the pit was emptied and filled with approximately 2" of water. Feed and water were provided *ad libitum* and intake was recorded.

Each chamber was equipped with a ventilation system connected to a dehumidifying air conditioner at the air inlet, an exhaust fan, and an air flow meter using ultrasound speed measurements (Panametrics, Waltham, MA). Air samples were taken from air inlets (for background corrections) and outlets for 3.75 minutes every 15 minutes. Sampled air was pulled through an 84-meter gas cell (Gemini, Anaheim, CA) connected

to a Magna 760 Fourier Transform Infrared (**FTIR**) Spectrometer (Nicolet, Madison, WI). Using the FTIR, ammonia was quantified in both inlet and exhaust air. The experimental period consisted of one week adaptation followed by one week of data collection. During the data collection period, ammonia emission data were collected on Days 2, 4, and 6 for 24 h each day. In addition, samples were taken on Day 5 for olfactometry and odorant analysis using GC-MS at Iowa State University.

Table 2. Calcium and phosphorus sources used in each of the trials in Experiment 2. Diets were formulated to meet or exceed NRC (1998) recommendations.

	Control	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
Calcium carbonate	X					
Calcium sulfate		X	X	X	X	X
Calcium chloride						X
Dicalcium phosphate	X	X				
Monocalcium phosphate					X	X
Phosphoric acid			X	X		

Experiment 3: Impact of acidogenic agents on growth performance. To determine the impact of diets that reduced ammonia emission on growth performance, 90 nursery pigs (45 barrows and 45 gilts) were assigned each to either a control diet containing dicalcium phosphate and calcium carbonate, or this diet but formulated with phosphoric acid and calcium sulfate, or the control diet but with monocalcium phosphate and a mixture of calcium sulfate and calcium chloride (see Table 3). Pigs were blocked by body weight and housed three per pen. Growth performance was monitored over a three-week period.

Table 3. Composition of diets as used in Exp. 3. (%)

Items	**Control**	**Monocalcium phosphate**	**Phosphoric acid**
Blood meal	2.00	2.00	2.00
Corn	58.48	58.21	56.59
Fish meal	2.50	2.50	2.50
Soybean meal (48%)	23.31	23.31	23.31
Whey	6.43	6.43	6.43
Lysine HCl	0.15	0.15	0.15
Threonine	0.12	0.12	0.12
Methionine	0.18	0.18	0.18
Dicalcium phosphate	1.34		
Monocalcium phosphate		**1.18**	
Phosphoric acid			**1.08**
Limestone	0.71		
Calcium sulfate		**0.49**	**2.85**
Calcium chloride		**0.65**	
Salt	0.40	0.40	0.40
Copper sulfate	0.10	0.10	0.10
Vit./min. premix	0.25	0.25	0.25
Antibiotics	0.05	0.05	0.05
Poultry fat	4.00	4.00	4.00

V. Results:

General: There were no problems in animal health in experiment 1. In experiment 2 and 3, mild diarrhea was occasionally observed in animals on diets with calcium sulfate.

Experiment 1: Impact of acidogenic agents on urine pH. Urine pH was decreased (P<.05) by approximately 1 pH unit in animals consuming diets containing phosphoric acid (H_3PO_4) & calcium sulfate and monocalcium phosphate & calcium sulfate compared to urine pH from animals receiving the control diet (Figure 1). However, the hydrochloric acid diet (**HCl**), which had a lower diet pH than others (Table 1), did not affect urine pH.

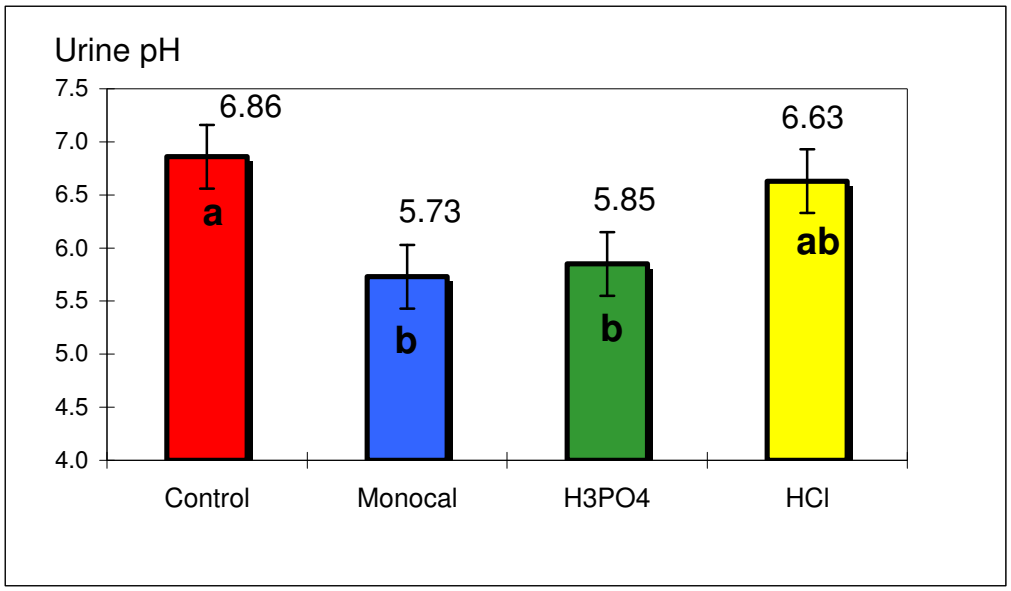

Figure 1. Urine pH results from Exp. 1.

Experiment 2: Impact of acidogenic agents on ammonia and odor emissions. Based on the results of Exp. 1, a series of environmental chamber trials were performed for the determination of ammonia and odor emission as affected by the different dietary calcium and phosphorus sources (Table 2). Grower (G) pigs fed the phosphoric acid & calcium sulfate diet had significantly decreased ammonia emission compared to the control diet (Figure 2). The ammonia reduction for the phosphoric acid (grower) diet were approximately 30%. Also, the monocalcium phosphate & calcium sulfate & calcium chloride diet decreased ammonia emission by approximately 17%. However, other treatments (calcium sulfate and monocalcium phosphate & calcium sulfate) did not affect ammonia emission.

Surprisingly, monocalcium phosphate & calcium sulfate, which substantially reduced urine pH in Experiment 1, did not affect ammonia emission. It is hypothesized that the excess calcium sulfate (excess SO_4^{2-} ions) may have reduced the dietary electrolyte balance too much with negative consequences for animal health. Also, this calcium sulfate may have induced adverse effects on nutrient availability due to the abnormal ion balance in the intestine (mild diarrhea was observed in these pigs). Replacing a portion of the calcium sulfate with calcium chloride did result in a reduction in ammonia emission. As the phosphoric acid does not supply any calcium, in contrast to monocalcium phosphate, the amount of calcium sulfate in the phosphoric acid diet is actually higher than in the monocalcium diet. Nevertheless, diarrhea problems were not observed in these animals and ammonia emission was reduced.

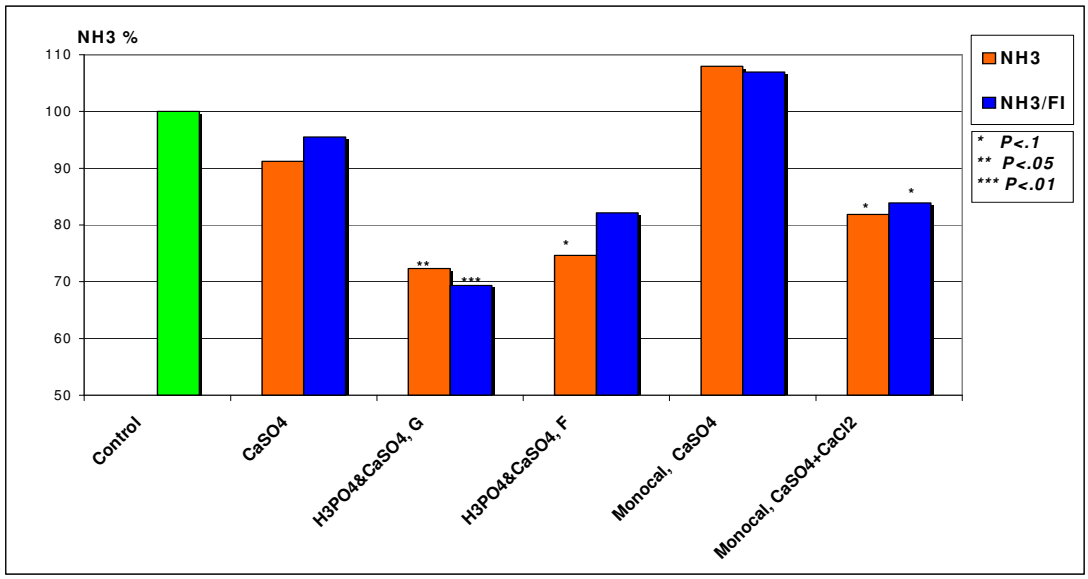

Fig. 2. Ammonia emission in exhaust air, relative to that observed for pigs fed a control diet. NH3/FI is ammonia emission corrected for feed intake differences between treatments, G is grower, F is finisher.

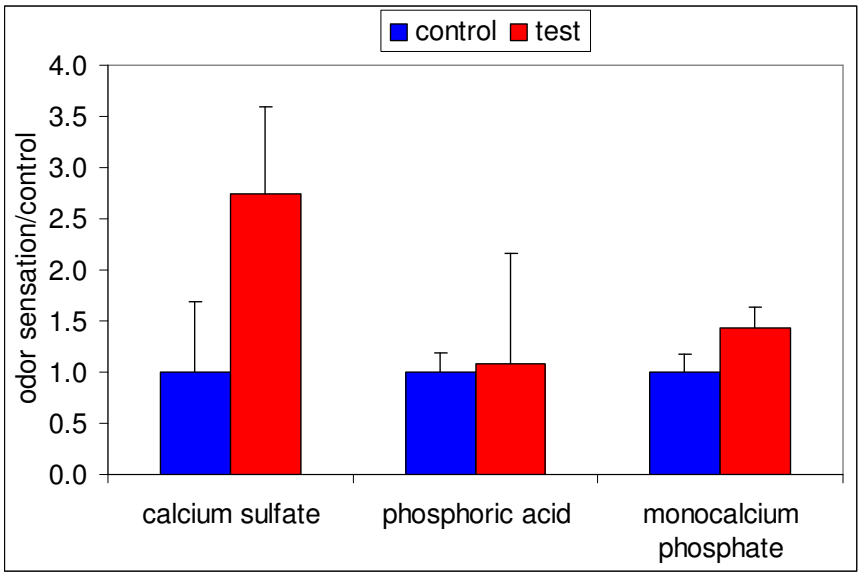

Fig. 3. Odor dilution threshold of exhaust air from pigs fed test diets relative to that observed in exhaust air from pigs fed control diets.

Odor in exhaust air was assessed using olfactometry and by adhering odorants to micro-fibers that were subsequently analyzed using GC-MS. The olfactometry data are summarized in Figure 3, and the GC-MS data are summarized in Figure 4. Calcium sulfate resulted in a numerical increase in odor sensation relative to the control (P=0.13), in line with the observation that animals on this diet experienced diarrhea and in line with the suggestion that nutrient digestion is less complete in diets with calcium sulfate (as observed in Experiment 1; data not shown). For this same diet, significant increases in phenolics and volatile fatty acid emissions were observed (Figure 4). These compounds are important contributors to odor emission and this finding supports the finding in Figure 3 that calcium sulfate increased odor.

Phosphoric acid and monocalcium phosphate did not affect odor sensation as determined using olfactometry. Similarly, no effects of phosphorus source on odorant

concentration in air were observed (Figure 4). These data suggest that feeding such diets has little impact on odor emission.

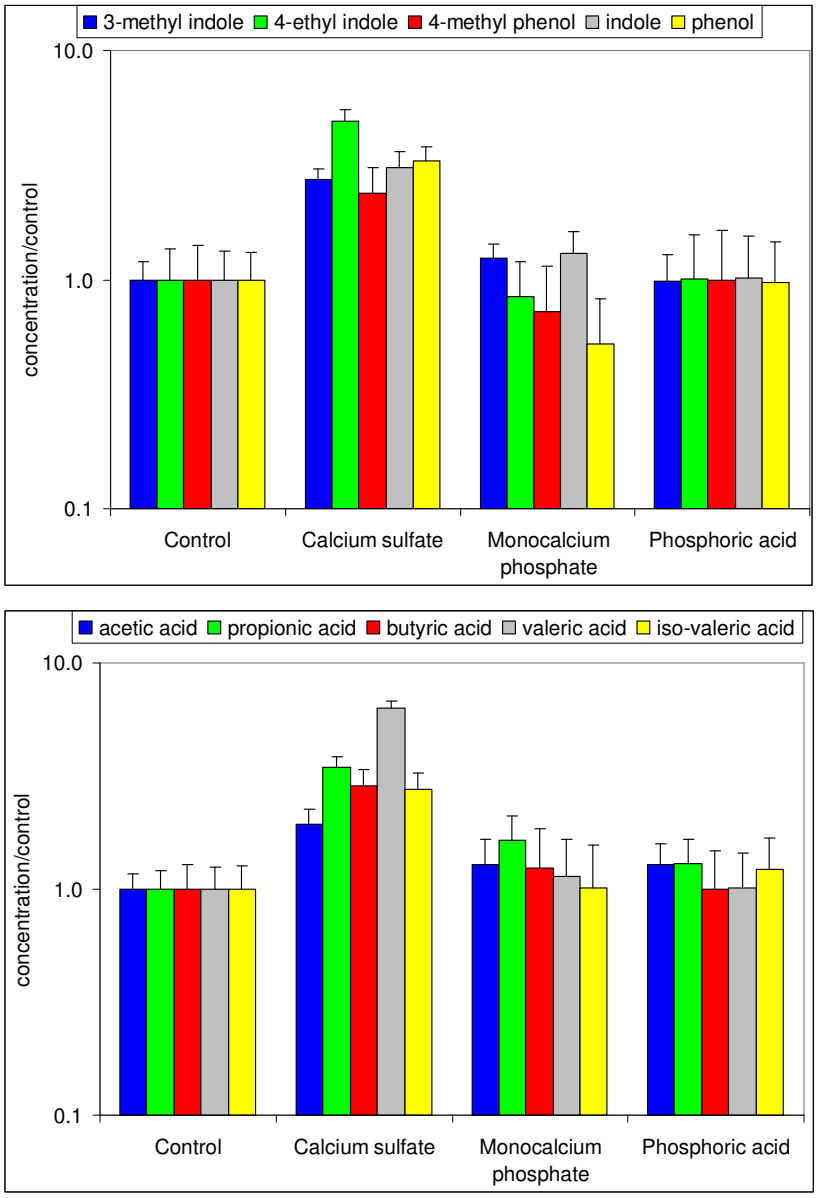

Figure 4. Odorant concentration in exhaust air as determined using GC-MS. Top panel: phenolics, bottom panel: volatile fatty acids.

Experiment 3: Impact of acidogenic agents on growth performance. Growth performance was measured in nursery pigs as the sensitivity to electrolyte imbalance is expected to be most pronounced in this category of pigs. The results of this experiment are summarized in Table 4.

Both test diets led to a decrease in feed intake and, as a result, a decrease in average daily gain. Feed efficiency was statistically not affected although a trend was seen for a worsened feed/gain ratio. Several researchers have evaluated monocalcium phosphate and phosphoric acid as feed ingredients and have observed no negative effects on performance (e.g., Ludke and Schone, 1991, Roth and Kirchgessner, 1989). It is thus more likely that the calcium sources are responsible for these problems, in line with observations from Jongbloed (personal communication).

Table 4. Growth performance results as observed in Experiment 3.

	Control	Phosphoric acid & calcium sulfate	Monocalcium phosphate and calcium sulfate/chloride mix	Sem
ADG (kg/day)	0.580[a]	0.538[b]	0.492[c]	0.014
ADFI (kg/day)	0.827[a]	0.784[a]	0.723[b]	0.019
F/G ratio	1.409	1.473	1.472	0.037

[a,b,c] Means within the same row lacking a common superscript letter differ (P<.05)

In conclusion, lowering urine pH through the use of phosphoric acid and monocalcium phosphate is technically feasible, and this reduction will lead to a decrease in ammonia emission. However, in order for these phosphorus sources to have maximal efficacy, sources of calcium other than calcium carbonate (limestone) need to be utilized. In this experiment, calcium sulfate and calcium chloride were used for this purpose, but they were found to be unsatisfactory, and an exhaustive study of literature has not yielded any calcium salts that are *and* acidogenic *and* suitable for use in animal nutrition.

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