

Effects of Different Dietary Acidifier Sources of Calcium and Phosphorus on Ammonia, Methane and Odorant Emission from Growing-finishing Pigs*

I. B. Kim¹, P. R. Ferket², W. J. Powers³, H. H. Stein⁴ and T. A. T. G. van Kempen**

Department of Animal Science, North Carolina State University, Raleigh, NC 27695, USA

ABSTRACT : The objective of this study was to investigate the effects of different sources of Ca and P on urine and ileal digesta pH, and ammonia (NH₃), methane (CH₄), and odor emission. In experiment 1, eight pigs (commercial three-way cross; initial BW 67±3 kg) were arranged in a repeated 4×4 Latin Square design. All pigs were equipped with a T-cannula in the distal ileum. Four corn-soybean meal based diets were formulated. Diet 1 was the control in which dicalcium phosphate (DCP) and limestone (CaCO₃) were used as the sources of inorganic P and Ca. In Diets 2 and 3, H₃PO₄, monocalcium phosphate (MCP), and CaSO₄ replaced DCP and CaCO₃ as the inorganic sources of P and Ca. Diet 4 was similar to Diet 1 except that it was fortified with HCl to provide an acid load similar to that of diet 2. Urine and ileal digesta pH were determined in pigs fed each of these diets. In Exp. 1, urine pH decreased (p<0.05) in animals consuming diets containing H₃PO₄-CaSO₄ (5.85±0.38) and MCP-CaSO₄ (5.73±0.30) compared with the DCP-CaCO₃ diet (6.89±0.24). In the pigs consuming H₃PO₄-CaSO₄, ileal digesta pH decreased compared with the control (5.52±0.28 vs. 6.66±0.17; p<0.05). Based on the results of Exp. 1, a total of four trials were performed in environmental chambers for determining how NH₃, CH₄, and odor were affected by the different dietary Ca and P sources (Exp. 2). In Exp. 2, pigs fed the H₃PO₄-CaSO₄ diet had decreased (30%) NH₃ emissions compared with the control (p<0.05). Also, a combination of MCP-CaCO₃-CaCl₂ decreased NH₃ emission by 15% (p<0.05). Emission of CH₄ was decreased only with the H₃PO₄-CaSO₄ diet with 14% (p<0.05). Odorant emission of phenolics and volatile fatty acids increased roughly three-fold with the DCP-CaSO₄ diet but was not affected by other test diets. In conclusion, acidogenic Ca and P sources in swine diets can decrease the urinary pH and reduce NH₃ and CH₄ emission from swine facilities. (*Asian-Aust. J. Anim. Sci.* 2004, Vol 17, No. 8 : 1131-1138)

Key Words : Ammonia, Methane, Odor, Phosphorus, Calcium, Acidifiers, Pigs

INTRODUCTION

Swine production is associated with the emission of methane (CH₄) and ammonia (NH₃). Ammonia contributes to acid rain promoting eutrophication of surface waters (Likens et al., 1996). Methane contributes to the accumulation of greenhouse gases and livestock have been reported to contribute 50% of the CH₄ emission in the United States, included swine operations (USEPA, 1992).

An effective method for reducing NH₃ volatilization during land application of animal slurry is acidification prior to surface spreading (Pain et al., 1987; Stevens et al., 1989) as the reduced slurry pH results in the sequestration of NH₃ as non-volatile ammonium (NH₄⁺). However, slurry acidification has no effect on emissions from the barn.

An approach for reducing NH₃ emission in hog barns is to reduce the pH of urine, which reduces NH₃ emission from the surface of the slats (van Kempen, 2001). Also, Mroz et al. (2000) suggested that NH₃ emission from the barn could be reduced by reducing the dietary acid-base balance or by reducing the buffering capacity as a means to acidify urine. This can possibly be achieved through the calcium and phosphorus sources in the diet, as they are important dietary components governing urinary pH (Patience et al., 1987). The objective of this experiment was to evaluate the impact of dietary acidifier inclusion of dicalcium phosphate, monocalcium phosphate, or phosphoric acid in combination with calcium carbonate, calcium sulfate, and/or calcium chloride on ammonia, methane, and odor emission.

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** Corresponding Author: Theo van Kempen. Tel: +1-919- 515-4016, Fax: +1-919-515-7780, E-mail: T_vankempen@ncsu.edu

¹ SunJin Co., LTD., Seoul 151-054, Korea.

² Department of Poultry Science, North Carolina State University, Raleigh, NC 27695, USA.

³ Department of Animal Science, Iowa State University, Ames, IA 50011, USA.

⁴ Department of Animal Science, South Dakota State University, Brookings, SD 57007, USA.

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MATERIALS AND METHODS

General

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

Experiment 1

Eight castrated crossbred finishing pigs (Landrace×Yorkshire×Large White, commercial breed; initial body weight (BW) 67±3 kg) surgically fitted with cannulas at the

Table 1. Composition of the experimental diets as used in Exp. 1 for studying the impact of dietary Ca and P sources on urine and ileal pH (% as-fed basis)

Items	Treatments			
	Control DCP-CaCO ₃	MCP-CaSO ₄	H ₃ PO ₄ -CaSO ₄	DCP- CaSO ₄ -HCl
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 (DCP)	1.10	-	-	1.10
Monocalcium phosphate (MCP)	-	0.97	-	-
Phosphoric acid ¹	-	-	0.81	-
Calcium carbonate	0.85	-	-	-
Calcium sulfate ²	-	1.75	2.50	1.39
Hydrochloric acid	-	-	-	0.47
Salt	0.35	0.35	0.35	0.35
Vitamin-mineral premix ³	0.24	0.24	0.24	0.24
Cellulose	1.36	0.59	-	0.35
Chromic oxide	0.50	0.50	0.50	0.50
Chemical composition ⁴				
ME (kcal/kg)	3,462	3,462	3,462	3,462
Crude protein (%)	13.6	13.6	13.6	13.6
Calcium (%)	0.62	0.62	0.62	0.62
Total phosphorus (%)	0.52	0.52	0.52	0.52
Lysine (%)	0.66	0.66	0.66	0.66
Methionine (%)	0.23	0.23	0.23	0.23
Threonine (%)	0.51	0.51	0.51	0.51
Diet pH ⁵	5.54	5.19	3.98	3.59

¹ Feed grade. Potash Corporation of Saskatchewan, Inc., Chicago, IL. ² Feed grade. Archer Daniels Midland, Chicago, IL.

³ Provided the following per kilogram of diet: vitamin A, 6,358 IU; vitamin D₃, 636 IU; vitamin E, 50 IU; vitamin K, 1.91 mg; riboflavin, 4.81 mg; niacin, 14.41 mg; d-pantothenic acid, 14.41 mg; vitamin B₁₂, 21.195 µg; Zn, 115 mg; Fe, 230 mg; Mn, 19.2 mg; Cu, 9.6 mg; I, 0.29 mg; and Se, 0.29 mg.

⁴ Calculated values based on NRC (1998).

⁵ Determined as follows: 100.0 g of each diet sample was mixed and stirred with 500 ml distilled water in 1,000 ml volume beaker. The pH value was taken in supernatant after settling for 30 min.

Table 2. Treatments in Exp. 2 for evaluation of the impact of dietary Ca and P source on odorant emission

Items	Treatments
Control	
Ca	Calcium carbonate (CaCO ₃)
P	Dicalcium phosphate (DCP)
Trial 1	
Ca	Calcium sulfate (CaSO ₄)
P	Dicalcium phosphate (DCP)
Trial 2	
Ca	Calcium sulfate
P	Phosphoric acid (H ₃ PO ₄)
Trial 3	
Ca	Calcium sulfate
P	Monocalcium phosphate (MCP)
Trial 4	
Ca	Calcium carbonate (CaCO ₃) Calcium chloride (CaCl ₂)
P	Monocalcium phosphate

distal ileum were used to study the effects of diet composition on ileal and urine pH. The pigs were housed in individual pens and received water *ad libitum*. Feed was provided twice daily in the amount of 45 g/kg BW^{0.75} per meal, nearly three times the maintenance requirement.

Four experimental diets (Table 1) were formulated to meet or exceed the nutrient requirements of finishing barrows following NRC (1998) guidelines. These diets were based on conventional sources of calcium (Ca) (calcium carbonate, CaCO₃; Ca 38.5%) and phosphorus (P) (dicalcium phosphate, DCP; Ca 22.0%, P 18.5%) as the negative control, or acidogenic calcium (calcium sulfate (CaSO₄; Ca 21.8%)) and phosphorus (monocalcium phosphate (MCP; Ca 17.0%, P 21.1%)) or phosphoric acid (H₃PO₄; P 26.9%) sources. To provide a positive control, the diet containing the conventional calcium and phosphorus sources was fortified with hydrochloric acid (HCl) such that dietary pH was reduced and dietary acidity was greater than with the phosphoric acid containing diet.

Each period consisted of a five-d adaptation period to the diet, followed by a two-d sample collection period. Urine was collected in the morning immediately upon voiding, and ileal juices were collected from 7 to 8 am by attaching bottles to the cannulas. Sample pH was determined the pH after cooling to room temperature (23°C) using a glass electrode (Fisher Accumet[®] pH meter Model 610A with a Orion 8104 Ross[®] Combination pH electrode, Ambler, PA) directly submerged in the sample.

Table 3. Composition of the experimental diets used in Exp. 2 (% as-fed basis) for evaluation of the impact of dietary Ca and P source on odorant emission

Items	Treatments				
	Control DCP-CaCO ₃	DCP-CaSO ₄	H ₃ PO ₄ -CaSO ₄	MCP-CaSO ₄	MCP-CaCO ₃ -CaCl ₂
Ground corn	73.00	72.46	71.17	72.34	72.96
Soybean meal (CP 48%)	22.57	22.57	22.64	22.57	22.57
Corn oil	2.00	2.00	2.30	2.00	2.00
Dicalcium phosphate (DCP)	0.80	0.80	-	-	-
Monocalcium phosphate (MCP)	-	-	-	0.65	0.65
Phosphoric acid ¹	-	-	0.61	-	-
Calcium carbonate	0.85	-	-	-	0.52
Calcium sulfate ²	-	1.39	2.50	1.66	-
Calcium chloride ³	-	-	-	-	0.67
Salt	0.50	0.50	0.50	0.50	0.50
Vitamin-mineral premix ⁴	0.25	0.25	0.25	0.25	0.25
L-lysine-HCl	0.03	0.03	0.03	0.03	0.03
Chemical composition ⁵					
ME (kcal/kg)	3,428	3,409	3,387	3,405	3,422
Crude protein (%)	16.8	16.8	16.7	16.7	16.8
Calcium (%)	0.58	0.58	0.58	0.57	0.57
Total phosphorus (%)	0.51	0.51	0.51	0.50	0.50
Lysine (%)	0.90	0.89	0.90	0.89	0.90
Methionine (%)	0.28	0.27	0.27	0.27	0.28
Threonine (%)	0.63	0.63	0.63	0.63	0.63

¹ Feed grade. Potash Corporation of Saskatchewan Inc., Chicago, IL. ² Feed grade. Archer Daniels Midland, Chicago, IL.

³ Feed grade. Dow Agriculture Co. Inc., Des Moines, IA.

⁴ Provided the following per kilogram of diet: vitamin A, 6,623 IU; vitamin D₃, 662 IU; vitamin E, 52 IU; vitamin K, 1.99 mg; riboflavin, 5.01 mg; niacin, 15.01 mg; d-pantothenic acid, 15.01 mg; vitamin B₁₂, 22.08 µg; Zn, 120 mg; Fe, 240 mg; Mn, 20.0 mg; Cu, 10.0 mg; I, 0.30 mg; Se, 0.30 mg.

⁵ Calculated values based on NRC (1998).

* Provided the following per kilogram of diet: vitamin A, 6,358 IU; vitamin D₃, 636 IU; vitamin E, 50 IU; vitamin K, 1.91 mg; riboflavin, 4.81 mg; niacin, 14.41 mg; d-pantothenic acid, 14.41 mg; vitamin B₁₂, 21.195 µg; Zn, 115 mg; Fe, 230 mg; Mn, 19.2 mg; Cu, 9.6 mg; I, 0.29 mg; Se, 0.29 mg.

Experiment 2

Based on the results of Exp. 1, environmental chamber trials were conducted to determine how NH₃, CH₄, and odorants emission were affected by the different dietary Ca and P sources (Table 2). The experiment was carried out using a cross-over design; the treatment schedule for Chamber 1 was A-B-A-C and for Chamber 2: B-A-C-A, with A being the control treatment, and B and C being treatment diets. One group of animals with a starting BW of approximately 25 kg and end weight of approximately 70 kg was used for each sequence. Treatments were tested over 2 wk periods during which animals were allowed to adapt to the diet for 1 wk. During the following week, emissions were monitored.

The chambers used were 2.1×2.7×2.4 m³ (width×length×height) and contained a pigpen of 2.1×2.4 m² positioned above a pit designed for pit-recharge (emptied weekly and precharged with 120 L water). Each chamber housed 10 crossbred barrows on concrete slats. Feed was provided *ad libitum* through a two-hole stainless steel feeder and water through a water nipple equipped with a flow meter. The control and experimental diets (Table 3) were formulated to meet the nutrient requirements for grower barrows (NRC, 1998). Chambers were maintained at approximately 25°C.

The airflow through the chamber was 150±1.5 m³/h per chamber, measured using Panametrics GM868 ultrasonic flow probes (Panametrics, Waltham, MA). As airflow was fixed, relative differences in concentration equate to relative differences in emission.

To determine CH₄ and NH₃ emissions, air was sampled at 15 min intervals for three 24 h periods, spaced 24 h apart. During each 15 min sampling interval, air was sampled from the inlet, chamber A and chamber B, each for 3.75 min. During sampling, 65 L of air per min was drawn through a Saturn variable path-length gas cell (set to 84 m; Gemini, Anaheim, CA) connected to a Magna 760 Fourier Transform Infra Red spectrometer equipped with a liquid-nitrogen cooled Mercury-Cadmium-Telluride (MCT-B) detector (Nicolet, Madison, WI). Infrared spectra were obtained by scanning the sampled air from 4,000 to 740 cm⁻¹ at a resolution of 0.5 cm⁻¹; the background used for these spectra was obtained by scanning air entering the chambers. Each spectrum consisted of 64 scans collected after an 80 second equilibration of the gas cell. Ammonia was quantified by measuring the area under the peak between 909.7 and 906.1 cm⁻¹ and methane was quantified by measuring the area under the peak between 2,951.0 and 2,946.5 cm⁻¹ (based on reference spectra obtained from the

Table 4. Urine and ileal digesta pH as affected by dietary calcium and phosphorus sources (Exp. 1, DCP is dicalcium phosphate, MCP is monocalcium phosphate)

Items	Treatments			
	Control DCP-CaCO ₃	MCP-CaSO ₄	H ₃ PO ₄ -CaSO ₄	DCP-CaSO ₄ -HCl
Urine pH	6.89±0.24 ^a	5.73±0.30 ^b	5.85±0.38 ^b	6.63±0.35 ^{ab}
Ileal digesta pH	6.66±0.17 ^a	6.69±0.22 ^a	5.52±0.28 ^b	6.05±0.25 ^a

^{a, b} Means in the same row lacking a common superscript were different ($p < 0.05$).

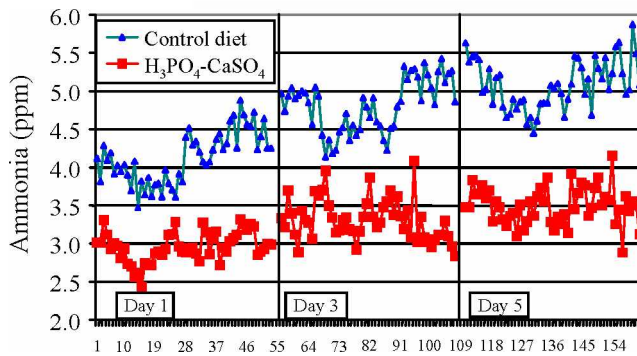


Figure 1. Example of ammonia emission pattern observed over time in Exp. 2 (Control vs. H₃PO₄-CaSO₄). Air samples were analyzed at 15 min. intervals.

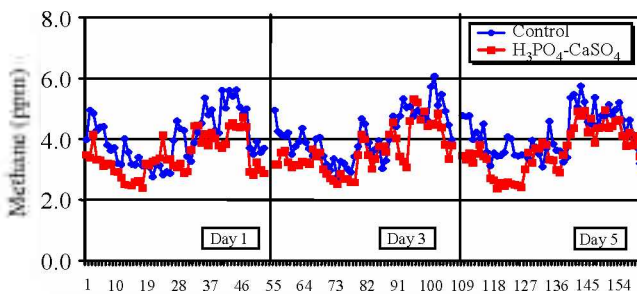


Figure 2. Example of methane emission pattern over time in Exp. 2 (Control vs. H₃PO₄-CaSO₄). Air samples were analyzed at 15 min. intervals.

EPA). Due to a technical problem, air samples were collected only for a total of 48 h in trial 1.

Twice weekly air samples were also collected in 10L Tedlar bags (manufactured at Iowa State University) and odorants were adhered to 75 μ m polydimethylsiloxane/carboxen Solid Phase Micro-Extraction (SPME) fibers (Supelco, Bellefonte, PA) with an adsorption time of 20 min. These samples were shipped overnight to Iowa State University where they were analyzed using dynamic forced-choice olfactometry for odor, a Jerome meter for H₂S, and a gas chromatograph-mass spectrometer for odorants (Huang et al., 1996; Gralapp et al., 2001, 2002).

Experimental design and statistical analysis

The pH data from Exp. 1, and the olfactometry, and odorant results from Exp. 2 were analyzed using analysis of variance with treatment means being separated using a least significance test using SAS (1992). The ammonia and

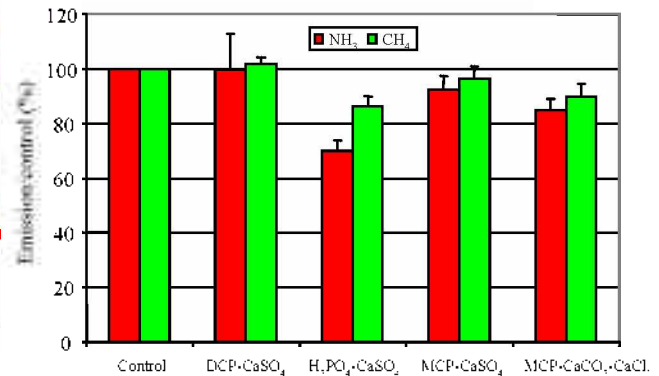


Figure 3. Ammonia and methane emission, relative to that observed from pigs fed a control diet, as affected by dietary calcium and phosphorus source (Exp. 2).

methane data of Exp. 2 were subjected to analysis with the following mixed model (Littell et al., 1996):

$$Y_{ijk} = \mu + \alpha_i + \beta_j + \gamma_k + \tau_l + \omega_{ik} + (\alpha \times \tau)_{il} + (\gamma \times \tau)_{kl} + (\omega \times \tau)_{kil} + \epsilon_{ijk}$$

Where, Y_{ijk} = determined variable, μ = overall mean, α_i = the effect of dietary treatment ($i=1,2$), β_j = the effect of measuring day ($j=1,2,3$), γ_k = the environmental chamber ($k=1,2$), τ_l = the effect of time within a measuring day ($l=1 \dots 96$), ω_{ik} = initial BW, $(\alpha \times \tau)_{il}$ = interaction between dietary treatment and time, $(\gamma \times \tau)_{kl}$ = interaction between environmental chamber and time, $(\omega \times \tau)_{kil}$ = interaction between initial BW and time, and ϵ_{ijk} = random error associated with each determination.

RESULTS

In Exp. 2, mild diarrhea was observed in both groups of animals fed the diet based on DCP-CaSO₄. No other health problems were noted.

In Exp. 1, urinary pH decreased ($p < 0.05$) in animals consuming diets containing H₃PO₄-CaSO₄ (5.85±0.38) and MCP-CaSO₄ (5.73±0.30) compared with urinary pH from animals receiving the control diet (DCP-CaCO₃: 6.89±0.24; Table 4). Although numerically the hydrochloric acid-supplemented diet had the lowest dietary pH (Table 1), the urinary pH was not affected by the addition of HCl in the diet (6.63±0.34, $p > 0.05$). Only in the pigs consuming the H₃PO₄-CaSO₄ diet, ileal digesta pH was decreased

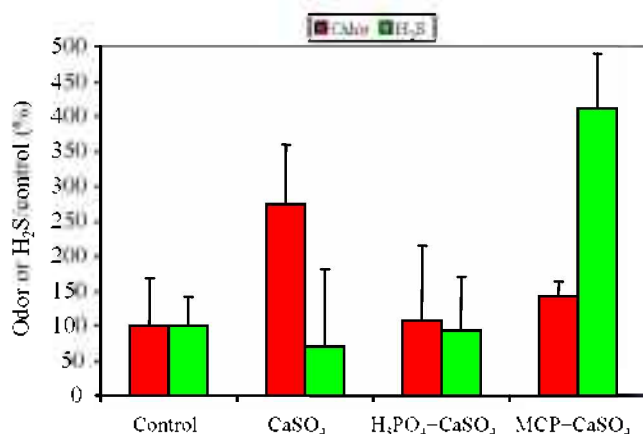


Figure 4. Odor dilution threshold and hydrogen sulfide concentration in exhaust air from pigs fed test diets relative to that observed in exhaust air from pigs fed diets formulated with alternative calcium and phosphorus sources (Exp. 2). The odor dilution threshold and the H₂S concentration for the controls was a 920 fold dilution and 0.51 ppm, respectively.

compared with the control diet (5.52 ± 0.28 vs. 6.66 ± 0.17 ; $p < 0.05$, Table 4).

Examples of the time course of ammonia and methane emission observed in Exp. 2 are provided in Figure 1 and 2, respectively. Pigs fed the H₃PO₄-CaSO₄ and the MCP-CaCO₃-CaCl₂ diets had significantly decreased NH₃ emission compared with pigs fed the control diet ($p < 0.05$, Figure 3). The NH₃ reduction (Figure 3) with the H₃PO₄-CaSO₄ diet and the MCP-CaCO₃-CaCl₂ diet were 30.3 and 15.3% lower, respectively, than the emission from pigs fed the control diet ($p < 0.05$). The DCP-CaSO₄ and the MCP-CaSO₄ did not affect NH₃ emission ($p > 0.05$). Methane emission from pigs fed the H₃PO₄-CaSO₄ diet was reduced by 13.6% ($p < 0.05$) compared with pigs fed the control diet. However, for all other dietary treatments, no differences in methane emission ($p > 0.05$) were observed.

Odor sensation was assessed using olfactometry (Figure 4) and odorants were measured by adhering odorants to micro-fibers that were subsequently analyzed using GC-MS (Gas Chromatograph-Mass Spectrophotometer; Figure 5). Due to a loss of samples in a shipment, insufficient data points for the MCP-CaCO₃-CaCl₂ diet were available. Therefore, only data for the remaining diets are presented.

The DCP-CaSO₄ diet resulted in a three-fold numeric increase in odor sensation relative to the control diet, but due to the large variation in panelist response this difference was not statistically significant ($p = 0.13$). For this same diet, significant increases in phenolic and volatile fatty acids (VFA) emissions were observed ($p < 0.05$; Figure 5), but not in H₂S (0.36 ± 0.56 vs. 0.51 ± 0.21 ppm for the control). These compounds are important contributors to odor emission and the increase in odorant concentration (other than H₂S) matched the numerical increase in odor sensation in Figure 4. The H₃PO₄-CaSO₄ and MCP-CaSO₄ diets did not affect

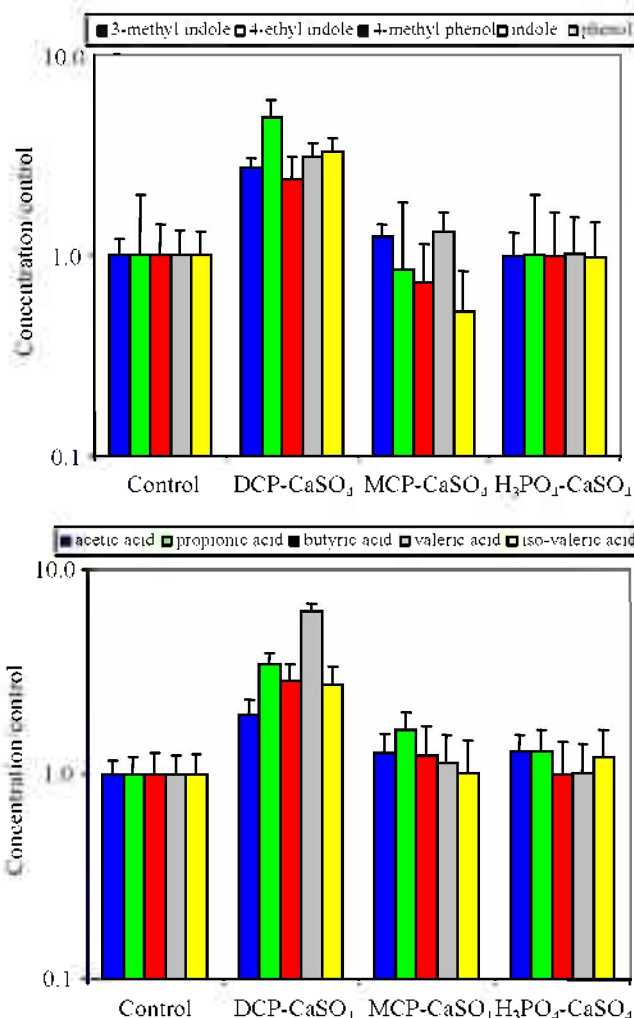


Figure 5. Odorant concentration in exhaust air as affected by dietary calcium and phosphorus sources (Exp. 2).

odor sensation as determined using olfactometry. Similarly, no effects of these diets on VFA or phenolic concentration in air were observed using GC-MS analysis (Figure 5). H₂S, however, was increased approximately four-fold with the MCP-CaSO₄ diet ($p < 0.05$) compared with the other three diets (Figure 4).

DISCUSSION

Urea from urine is the major precursor of ammonia in swine production. This urea is hydrolyzed by urease forming volatile ammonia (Muck and Steenhuis, 1981). The rate of volatilization of this ammonia is a function of pH, as ammonia and non-volatile ammonium are in a pH-dependent equilibrium. Reducing pH will thus decrease ammonia emission (Vlek and Stumpe, 1978; Sommer and Husted, 1995).

The pH value of slurry follows the same pattern as that observed for urinary pH (Canh et al., 1998b). Thus, acidogenic compounds that reduce urinary pH may be of

benefit for reducing ammonia emission, as shown by van Kempen (2001). A low dietary electrolyte balance can also decrease the pH of urine (Patience et al., 1987; Canh et al., 1998a, b; Mroz et al., 2000). For this study, acidogenic alternatives to commonly used feed ingredients were used for reducing urine pH. In Exp. 1, H_3PO_4 - $CaSO_4$ and MCP- $CaSO_4$ reduced urine pH by approximately 1 pH unit, confirming their role as acidogenic agents for pig diets. Surprisingly, HCl did not reduce urine pH, in contrast to observations of Okumura and Tasaki (1968). The reason for this lack of response with HCl dosing may be the physiological regulation of Cl⁻ retention and excretion in pigs' body (serum and tissues; Budde and Crenshaw, 2003).

Canh et al. (1998b) established the following regression equation between the natural logarithm (Ln) of ammonia emission and pH of urine:

$$\text{Ln}(\text{NH}_3 \text{ emission}) = 3.76 (\pm 0.11) + 0.22 (\pm 0.02) \times \text{Urine pH} \quad (R^2 = 0.84)$$

According to the equation above and our urine pH data, the H_3PO_4 - $CaSO_4$ and MCP- $CaSO_4$ diet should reduce the NH_3 emission by 41% and 44%, respectively, compared with the control diet. However, in Exp. 2, the H_3PO_4 - $CaSO_4$ diet reduced NH_3 emission by only 30% (Figure 3), while the MCP- $CaSO_4$ diet in Exp. 2 did not affect the NH_3 emission. Possibly because the equation of Canh et al. (1998b) was established for *in vitro* conditions, which ignores factors such as the extent of mixing of urine and feces *in vivo*, pen fouling, and pH raising effects of concrete, urine pH did not affect the *in vivo* NH_3 emission as much as the equation predicted. Similar findings were reported by van Kempen (2001).

The MCP- $CaSO_4$ diet resulted in a 1 pH unit reduction in urine pH in Exp. 1, but in Exp. 2, this diet did not significantly affect the NH_3 emission. In line with the problems with the DCP- $CaSO_4$ diet (mild diarrhea, increased H_2S), it is expected that the problem with the MCP- $CaSO_4$ diet is related to the large amount of sulfate in this diet, leading to a mild intestinal upset resulting in altered characteristics of the fecal material (Veenhuizen et al., 1992). To test whether $CaSO_4$ caused such a problem, a diet based on MCP but with a mixture of $CaCO_3$ and $CaCl_2$ was tested. $CaCl_2$ is known to suppress appetite (Yen et al., 1981), while $CaCO_3$ is alkalogenic. The objective of combining these two calcium sources was to attempt to minimize the negative effects of either. Indeed, the combination of calcium sources with MCP did reduce the NH_3 emission. However, the reduction observed was only half that observed with the H_3PO_4 - $CaSO_4$ diet, likely because the pH reducing effect of $CaCl_2$ was negated by the pH raising effect of $CaCO_3$.

Methane is the most abundant organic gas in the earth's

atmosphere, and CH_4 concentrations have increased globally at the rate of about 0.7% or 12 ppb/yr from 1984 to 1994 (IPCC, 1995). Methane affects tropospheric ozone, hydroxyl radicals and carbon monoxide concentrations, stratospheric chlorine and ozone chemistry, and because of its radiative forcing properties (infrared absorption or greenhouse effect), the earth's energy balance. The largest biogenic sources are rice production, accounting for about 11%; enteric fermentation in animals, 16%; and decomposition of wastes, 17% (including 5% from animal waste) (Harper et al., 1999; Chen et al., 2003).

Methane emission from swine houses with pit recharge originates predominantly from the large intestine (Kaspers et al., unpublished), where its production is a function of pH (Lana et al., 1998). In this study, the H_3PO_4 - $CaSO_4$ diet reduced ileal pH by one pH unit, moving it from nearly neutral to slightly acidic. pH was not measured in the large intestines, but these data suggest that the pH in the large intestines may well have been reduced by these diets leading to a reduction of methane production of 14%.

Primary odorous compounds are VFA, phenol, p-cresol, indole, and skatole (Schaefer, 1977) and hydrogen sulfide (Hobbs et al., 1995). Odorant emission results from anaerobic protein and carbohydrate degradation and sulfur reduction, with odorants being the end-products or/and intermediates of fermentative processes by anaerobic bacteria (Zhu and Jacobson, 1999). A proposed means of reducing odorant emission is to inhibit certain bacteria groups in the gastro-intestinal tract of pigs or alter the fermentation of existing bacteria. pH is an important factor for achieving this (Mackie et al., 1998), and the ileal pH data show that the H_3PO_4 - $CaSO_4$ diet reduced intestinal pH, while all test diets were expected to reduce manure pH, although slightly. Nevertheless, data from Exp. 2 suggest that feeding diets with different sources of Ca and P had little impact on odor and odorant emission (Figure 5), suggesting that the bacterial activity responsible for odorant production (Otto et al., 2003) was not affected by treatments. The exception was the DCP- $CaSO_4$ diet, which increased odorant emission (Figure 5). However, as pigs on this diet suffered from mild diarrhea, the increase in odorant emission is likely a result of an increase in substrate availability for microbial fermentation and pen fouling.

Hobbs et al. (2001) suggested that H_2S is the most potent odorant contributing to swine odor, and the feeding of a high sulfur diet is reported to augment the emission of hydrogen sulfide (Shurson et al., 1999). In this study, the test diets based on $CaSO_4$ contained more sulfur than the control diet. However, neither the DCP- $CaSO_4$ nor the H_3PO_4 - $CaSO_4$ diet increased hydrogen sulfide emission. In contrast, the MCP- $CaSO_4$ diet resulted in a four-fold increase in H_2S emission but odor emission was not increased. The discrepancy between this study and the work

of Hobbs and Shurson is likely caused by differences in manure storage. In this study, a pit-recharge system emptied weekly was used, while Hobbs and Shurson used deep-pit systems in which manure is typically stored over a longer period of time, at a higher concentration, and under conditions that are much more anaerobic, thus possibly more prone to the emission of hydrogen sulfide. This observation also matches field observations in North Carolina's pit flush barns where hydrogen sulfide has been found to not be a suitable indicator gas for swine odor (North Carolina Division of Air Quality, personal communication).

IMPLICATIONS

The use of CaSO_4 and H_3PO_4 as inorganic calcium and phosphorus sources in swine diets results in a reduction in intestinal and urine pH. Possibly through this reduction in pH, these calcium and phosphorus sources reduce ammonia (30%) and methane (14%) emission without negatively affecting odor.

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