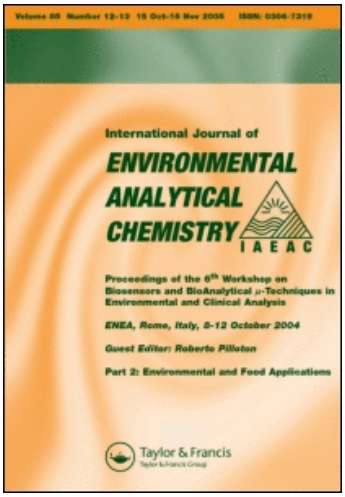

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ASSESSMENT OF AIRBORNE AMMONIA IN A SWINE FARMING ENVIRONMENT BY THE FLUORIMETRIC ENZYME METHOD

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Airborne ammonia in swine confinement facilities and in the exterior vicinity of confinement facilities was sampled in the breathing zone of farm workers and analyzed by the fluorimetric enzyme method. The results were compared against inter-laboratory results generated using an automated 'alkali-phenate to indophenol' method. Ammonia concentration in solution is reported in $\mu g.L^{-1}$ and in air is reported in ppbv.: Inter-method comparison by linear regression analysis yielded a correlation coefficient (R^2) of 0.99998, slope (a) of 0.9509 and intercept (b) at $-34.12\ \mu g.L^{-1}$. The t-values for the slope and intercept were 724.35 (t_a), and −0.7372 (t_b), with the critical values 4.673×10^{-16} (p_a) and 0.4888 (p_b) respectively for the 95% confidence level. The standard error for the slope and intercept were 0.0013 ($\sigma.a^{-1}$) and 46.2858 ($\sigma.b^{-1}$). The limit of detection for the fluorimetric enzyme method was 110 $\mu g.L^{-1}$ (3 σ) using field samples. The cumulative limit of detection for the airborne ammonia in the swine farming environment was 4 ppbv (300 L air). Ammonia concentration within the swine confinement facilities was in the range 1,000 to 10,000 ppbv and greater than the ambient atmospheric ammonia concentrations (1 to 5 ppbv). Ammonia levels outside of the swine confinement facilities was in the range 60 to 330 ppbv.

KEY WORDS: Airborne ammonia, swine farming environment, fluorimetry, enzymatic method, alkali-phenate method, environmental assessment.

INTRODUCTION

Respiratory tract irritation, rhinitis, sinusitis, bronchitis, asthma and odor related psychological symptoms are human sensitive determinants associated with hazardous chemicals generated in swine farming environment[1,2]. Volatile gaseous chemical species such as amines, carbon dioxide, methane and sulfides are produced in swine farms[3]. Among the prevalent swine farm gases and chemical species, ammonia (NH_3) is the primary irritant. Dose related ammonia-induced inflammatory response has been observed in pigs exposed to NH_3 up to 10,000 ppbv for 6 days, in an air-pollutant exposure chamber[4]. Exposure of plant workers to fertilizer chemicals such as urea, ammonia and diammonium phosphate resulted in significant obstructive lung changes affecting the larger airways and bronchospasm after long periods of exposure[5]. In swine farms, ammonia and ammonia generating chemical species such as uric acid, allantoin and urea

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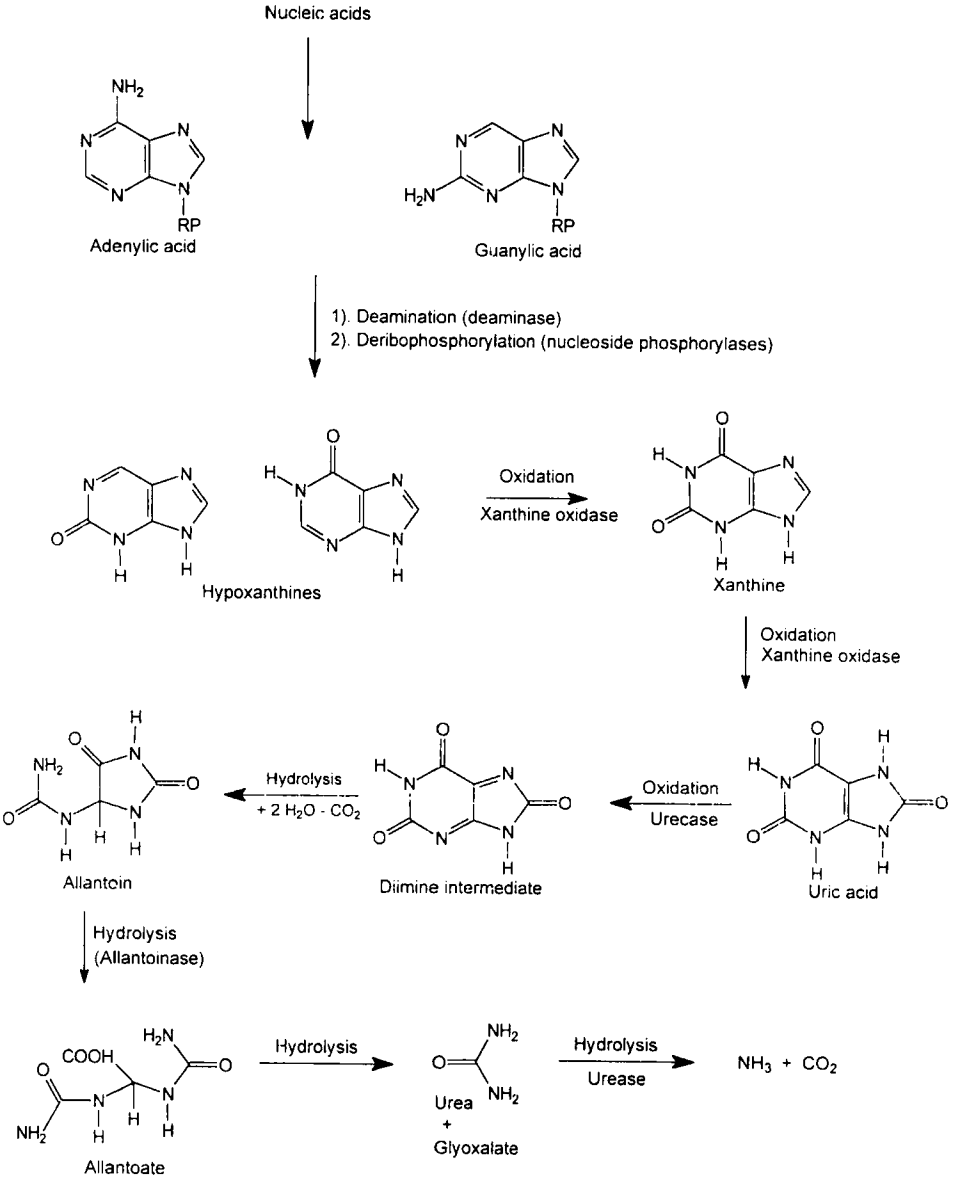
are prevalent and these metabolites are produced by the biological degradation of purine based nucleic acids. One such metabolic pathway is shown in scheme 1. Ammonia is also generated by the anaerobic degradation of proteins to amino acids. Sulfur compounds such as hydrogen sulfide and its derivatives such as mercaptans and mercaptides are major chemicals having repelling odor characteristics generated from swine farm slurry by the anaerobic degradation of sulfur enriched amino acids. Therefore, the air in the swine farming environment is a complex mixture containing nucleic acid degradation products such as ammonia and ammonia generating particulates, methane, mercaptans, mercaptides, endotoxins, β-1, 3-glucans, and viable and non viable bacterial residues. Hence, quantitation of ammonia from the swine farming environment requires an understanding of the reactivity of various chemical constituents present in the air and their possible interference in the analytical reaction matrix.

The 2 major analytical method groups for NH_3 involve: 1) separation of the matrix and the interferences from NH_3 or NH_4^+ ions; 2) NH_3 specific methods which do not involve the isolation of matrix. The matrix isolation method includes high performance liquid chromatography (HPLC) and ion chromatography (IC). Reverse phase HPLC method requires additional post column derivatization because NH_3 lacks chromophores in the uv-vis region to be monitored by photometric detection. Condensation reactions of NH_3 and other amines with aliphatic or aromatic aldehydes or ketones yield isoindoles. Isoindoles have high luminescence intensity and hence analysis of NH_3 by this method provides analytical sensitivity in the picomolar range[6]. Under alkaline pH conditions required for isoindole reaction, NH_3 generating particulates such as urea will hydrolyze to generate NH_3 resulting in report of falsely elevated levels of ammonia concentration. Advantages in using ion chromatography include the separation of NH_4^+ ion from other cations and quaternary-ammonium ions present in the sample matrix. Disadvantages of IC include: 1) an additional sample clean-up step involving solid phase extraction (SPE) to free the semi-volatile species and other organic species; 2) test samples containing NH_3 concentration above the column capacity will lead to prolonged column equilibrium time and possible damage due to overloading of other organic species present.

Ammonia specific methods without matrix isolation include spectrophotometry[7–10], electrochemistry[11,12], and chemiluminescence[13]. Ion selective electrode (ISE) lacks selectivity or specificity due to the interferences from other primary amines[12]. Under the ISE method conditions (alkali solution, pH > 12), urea undergoes hydrolysis and generates NH_3. However, in the enzymatic reaction method specific for NH_3, primary amines do not interfere[14–18]. The enzymatic method has been extensively investigated for the analysis of trace level ammonia in blood samples[17] containing urea up to 250 $mg.L^{-1}$. A photometric semi-automated enzyme method has also been employed in the analysis of lake water samples[19]. Analytical methods for NH_3 are reviewed and summarized in Table 1, along with the analytical reaction conditions and various environmental matrices from which NH_3 is analyzed.

Iowa is the largest swine producer in the United States of America (14×10^6 head, June 1, 1995) and the Iowa meat packing industry slaughters *ca.* 34.2×10^6 head per year. Large scale swine farming, in recent years, has become a concern to Iowans, because of occupational health of the workers, the health of residents living in the vicinity of swine farms, the pungent odor outside the swine confinements and other environmental pollution concerns (Cedar Rapid Gazette, January 7–9, 1996). We investigated the use of ammonia as a *'tracer-probe'* for monitoring airborne volatile species in swine farming environment, and as the parameter to quantify and evaluate a possible correlation between human symptoms and the airborne chemical species around swine farms. We have quantified the airborne ammonia concentration in the breathing zone of farm workers within swine confinement facilities and in the vicinity of

Scheme 1 Biological degradation of purine based nucleic acids to ammonia



confinement facilities by bubbling air through midget impingers containing sulfuric acid and analysis by fluorimetric enzyme method. The results were compared against inter-laboratory results generated using the automated 'alkali-phenate to indophenol' (APIP) method. Estimated ammonia concentrations from swine farming environments were compared with the literature data on ambient ammonia concentrations in the atmosphere and other industrial environments.

Table 1 Analytical methods summary for the analysis of ammonia samples from various environmental matrices.

Method	*Analytical Condition*	*Sample Matrice*	*Interferences*	*Detection Limit*	*Reference*
Cation Ion Exchange Chromatography-Post Column Fluorimetric Derivatization	pH: 10; Reaction with OPA/2-mercaptoethanol Automated analysis.	Sea water		85 pg (1.7 ng/mL)	6
Gas chromatography-Flame Thermionic Detection	Adsorption onto basic silica gel 15% PEG 6000/5% KOH on Chromosorb 103 (80/100) and curie point pyrolysis. Semi-automated analysis.	Atmospheric air (alkali treated silica column)		30 pg (20 pptv/2L	26
Chemiluminescence-Flow Injection Analysis	pH: > 12; NaOH solution containing free NaBr $2NH_3 + 3BrO^- \rightarrow N_2 + 3\ Br^- + 3\ H_2O$ Semi-automated analysis.	Rain water and Fog water	sulfite, nitrite, carboxylic acids, amino acids, urea, pyrogallol, humic acid	10.3 pg/mL	13
Cathodic Stripping Voltammetry	pH: 3.8; acetate buffer, RT.; $H_2C = O + NH_3 \rightarrow NH = CH_2 \rightarrow {}^+H_2N = CH_2$ ${}^+H_2N = CH_2 \rightarrow HN = CH_2$ (–0.85 V HMDE)	Sea water		230 pg (68 ng/mL)	11
Derivatization to Fluorophoric Compounds	Reaction of ammonia with Fluorescamine/sodium Lauryl sulfate impregnated filter paper and emission intensity measurement of the fluorophoric derivative; no extraction.	Work place air, diffusion to filter paper (passive monitors)		1 ppbv (8 hours)	24
Photometric Fiber Optic Sensor	pH: 8.0; phosphate buffer, silicone-caoutchouc polymer (immobilized with bromophenol blue indicator). Semi-automated analysis.	Environmental waters	carbonate, acetate, citrate	50 ng/mL	7
Photometric Alkali-salicylate-Indophenol Reaction	pH: 12.0, NaOH/citrate solution $[Fe(CN)_6]^{4-}$ catalyst Semi-automated analysis.	Natural fresh waters	urea, amino acids	1200 ng (60 ng/mL)	8, 9
Photometric Alkali-phenate-Indophenol Reaction	pH: > 10.8: $[Fe(CN)_6]^{4-}$ catalyst, RT.; Automated analysis.	Work place air, dynamic sampler (in 0.01 N H_2SO_4)		5 ng (25 ng/mL)	21
Photometric Alkali-phenate-Indophenol Reaction	pH: > 10.8, $[Fe(CN)_6]^{4-}$ catalyst, RT.; Automated analysis.	Swine farm air, dynamic sampler (in 0.01 N H_2SO_4)		48 ng (16 ng/mL)	This work
Photometric Enzyme Reaction	pH: 7.65; Tris buffer at 37°C; 80 U/300 µL GLDH enzyme. Semi automated analysis.	Lake water		1.9 ng (7.6 ng/mL)	19
Photometric Immobilized Enzyme Reaction	pH: 8.0; Phosphate buffer, RT; 80 U/mL GLDH enzyme. Automated analysis.	Food samples	No interference from amino acids	1.6 ng (85 ng/mL)	25
Fluorimetric Enzyme Reaction	pH: 8.0; Phosphate buffer, 8 U/14 nL GLDH enzyme.	Urine, Blood	No interference from urea	0.57 pg (69 ng/mL)	16
Fluorimetric Enzyme method	pH: 8.2; Phosphate-citrate buffer, RT, 23 U/2.7 mL GLDH enzyme.	Swine farm air, dynamic sampler (in 0.01 N H_2SO_4)		22 ng (110 ng/mL)	This work

EXPERIMENTAL

Reagents

Deionized water (18 mΩ) was collected from a NANOpure water system (Barnstead Thermolyne, Inc. IA). HPLC grade water (Optima), sodium dihydrogen phosphate and disposable fluorimetric cuvettes (1.0 × 1.0 × 4.5 cm) were purchased from Fisher scientific (Chicago, IL). Anhydrous citric acid, ammonia reagent kit, *l*-glutamate dehydrogenase and ammonia standards (5 $mg.L^{-1}$) were obtained from Sigma Diagnostics (St. Louis, MO). Sulfuric acid (5.0×10^{-3} M) was prepared in the laboratory and stored at 4°C, until use.

Sample collection

Air samples for ammonia were collected from different types of swine production facilities within Johnson and Lynn Counties of Iowa, in the United States of America. The types of swine farms included a traditional outdoor production facility, managed swine confinements (small, medium and large farms) and a swine-free animal house. Samples were collected in the workers' breathing zone (*ca.* 1.7 ± 0.3 m from the ground) during the day time between 08.00 to 17.00 hours. The sampling pumps were operated at 800 ± 25 $mL.min^{-1}$. Air samples (300 L) were collected by bubbling air through two midget impingers[20] connected in series, containing H_2SO_4 solution (5.0×10^{-3} M, 7.0 mL). Final solution volumes in the impingers were measured after air sampling (4.5 ± 0.5 mL), transferred to glass vials and stored at 4°C, until analysis.

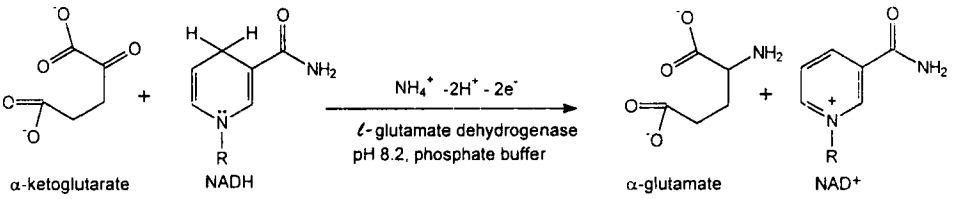
Eight composite samples were prepared for the inter-laboratory study from the following: field blanks (2 samples); indoor air samples from 5 replicates collected in two impingers connected in series (2 samples); outdoor air samples from 4 replicates collected in two impingers in series (2 samples); outdoor air sample from the swine free-control farm from 5 replicates collected in two impingers in series (2 samples).

Analysis

An automated APIP method was utilized for the inter-method comparison. The inter-method analysis was carried out at the University of Iowa Hygienic Laboratory (Des Moines, IA). Spectrophotometric measurements were carried out by the Sigma Diagnostics procedure[14] at 340 nm using an LKB Ultraspec II spectrophotometer. Emission intensity was measured on Hitachi F-1050 spectrofluorimeter. Emission intensity of NADH was measured at 460 ± 5 nm by setting the excitation monochromotor to 345 ± 5 nm. Both the excitation and emission wavelengths had fixed band width (15 nm). Reagent solution for the fluorimetric enzyme method was prepared by modification of the reagent kit received from Sigma Chemicals. The ammonia reagent was reconstituted in pH 8.2 buffer (monosodium phosphate, 10×10^{-3} M; and citric acid, 2.0×10^{-3} M). 6.0 mL of the reconstituted reagent was further diluted to 125 mL using the citrate-phosphate buffer. Final working solution contained the following reactants: NADH, 1.1×10^{-5} M; α-ketoglutarate 1.6×10^{-4} M; GLDH, 9.5×10^{3} $U.L^{-1}$. 2.5 mL aliquots of the working reagent were transferred to disposable cuvettes and the initial emission (E_i) measured following the incubation for 60 minutes, at ambient temperature.

The test solution, 200 µL (blank, standard, control or the unknown), was then added, and final emission intensity (E_f) measured after 60 minutes incubation. The difference in emission ($\Delta E = E_i - E_f$) was due to the consumption of NH_3 present in the test solution. Thus, ΔE was directly proportional to the number of moles of NH_3 reacted in the conversion of α-ketoglutarate to α-glutamate in the test solution as shown in scheme 2.

Scheme 2 *l*-glutamate dehydrogenase enzyme reaction.



RESULTS AND DISCUSSION

Analytical matrices

The observed linear calibration range for the fluorimetric enzyme method was 10 $\mu g.L^{-1}$ to 1,000 $\mu g.L^{-1}$ (Figure 1). The fluorimetric enzyme method was evaluated for three reagent matrices including water, H_2SO_4 (5.0×10^{-3} M) and citric acid (2.92×10 M^{-3}). No significant deviation in the recovery of NH_3 from citric acid solution was observed when compared to ammonia recovery from sulfuric acid solution (Figure 2), though positive interference due to the presence of citric acid has been reported previously[14]. Also, the measured ammonia concentration of the standards using the enzyme buffer containing citric acid was the same as the measured ammonia concentrations using the enzyme buffer having no citric acid. Citric acid in the enzyme reaction buffer has the advantage of preventing precipitation of trace metal hydroxides under the analytic reaction conditions (pH > 8.0). Sulfuric acid has been used as a liquid trapping reagent in dynamic samplers[21] (midget impingers) and in passive samplers[22] (cotton pads) for monitoring occupational exposure to NH_3, while citric acid and oxalic acid have found use as solid adsorbants in dynamic annular denuder tubes[23].

Inter-method results

The limit of detection for the fluorimetric enzyme method was 110 $\mu g.L^{-1}$ (3 σ), using the field samples. The determined cumulative limit of detection from 300 L air samples was 4 ppbv. The eight composite samples had ammonia in the concentration range 0.05 $mg.L^{-1}$ to 100 $mg.L^{-1}$. The enzymatic method results of the composite samples were plotted against the results obtained by the automated APIP method (Figure 3). Linear regression analysis for the inter-method results yielded correlation coefficient (R^2) of 0.99998, slope (a) of 0.9509 and intercept (b) at –34.12 $\mu g.L^{-1}$. The t-values for the slope and intercept were 724.35 (t_a), and –0.7372 (t_b), with the critical values 4.673×10^{-16} (p_a) and 0.4888 (p_b) respectively for the 95% confidence level. The standard error for the slope and intercept were 0.0013 ($\sigma.a^{-1}$) and 46.2858 ($\sigma.b^{-1}$). The analytical data from these two methods are well correlated and in good agreement. The slope less than unity

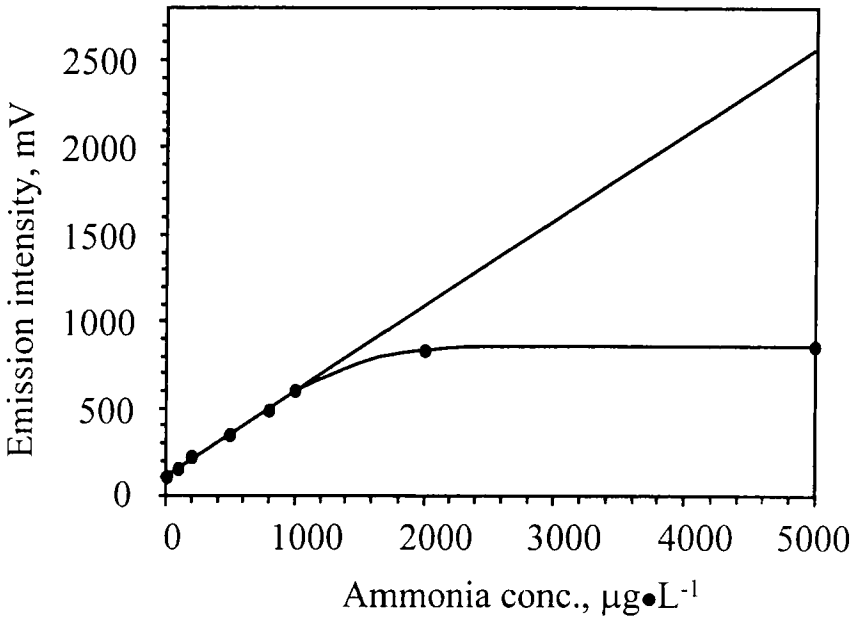


Figure 1 Reconstructed calibration graph for ammonia (10 to 5000 µg.L^{-1}). The enzyme reagent was prepared in pH 8.2 buffer containing sodium phosphate (5×10^{-3} M) and citrate (2×10^{-3} M).

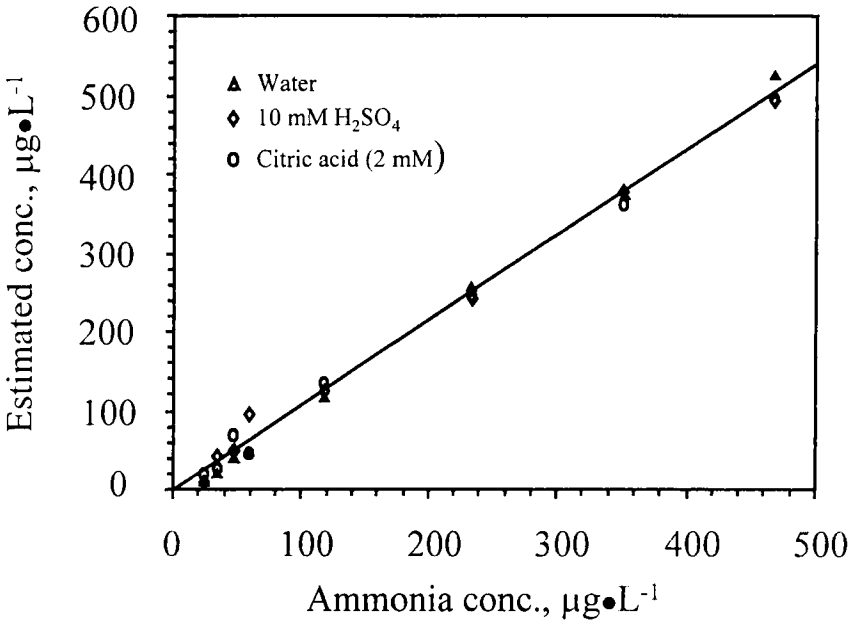


Figure 2 Analytical recovery of ammonia (10 to 500 µg.L^{-1}) from different matrices: water, H_2SO_4 (5×10^{-3} M) and citric acid (2×10^{-3} M). The enzyme reagent was prepared in sodium phosphate solution (5×10^{-3} M, pH 8.2).

(< 1.000) is accounted for by the higher NH_3 concentration estimated by the APIP method due to the hydrolysis of ammonia generating particulates.

The ammonia concentrations in the first and second impingers connected in series were determined. These results clearly demonstrate that there was no breakthrough of ammonia or ammonium particulates from the first impinger to the second impinger and that the trapping efficiency of H_2SO_4 solution (5.0×10^{-3} M) in the first impingers was greater than 99%. The estimated residual amount of NH_3 in the second impingers is very similar to the NH_3 levels estimated for the field blanks. Normalization of the cumulative field blank data suggests that the amount of ammonia present in the field blanks could account for up to 4 ppbv (300 L air). The lowest estimated NH_3 concentrations in this study are far greater (66 ppbv) than the field blank equivalent concentrations (4 ppbv).

The APIP method was used for inter-method comparison due to its wide acceptance for the analysis of ammonia from several matrices[8,10,19,21,28]. This method uses photometric

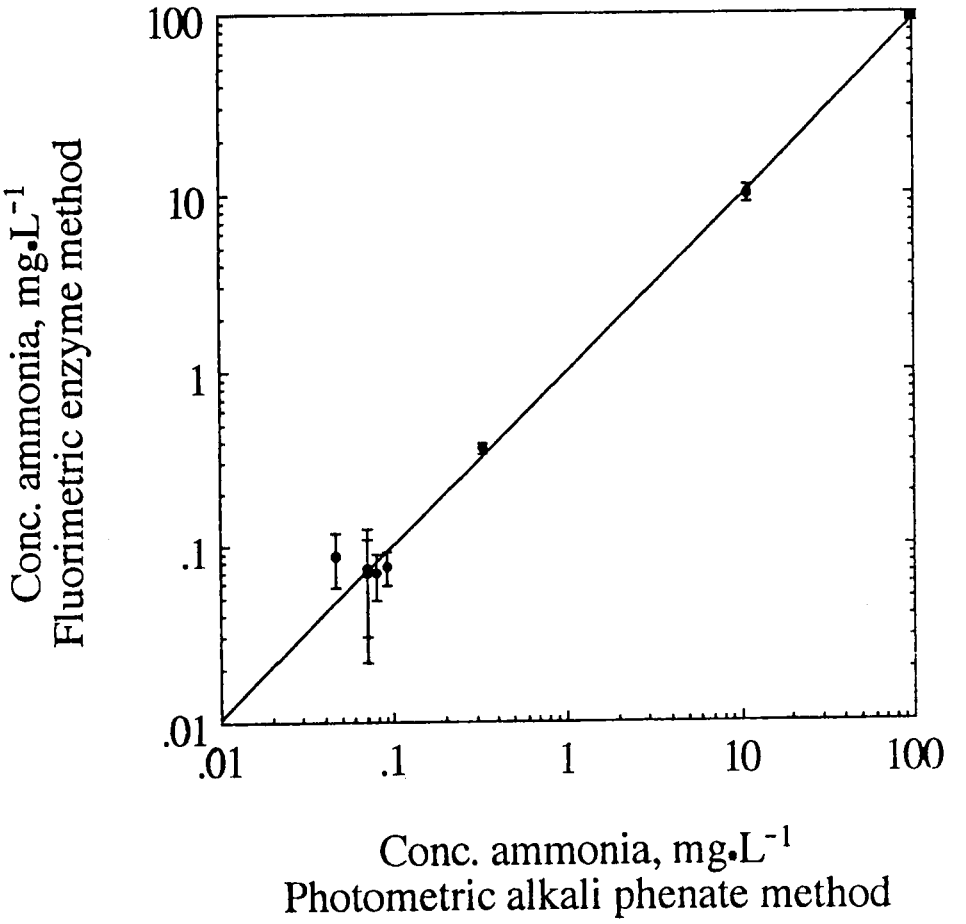
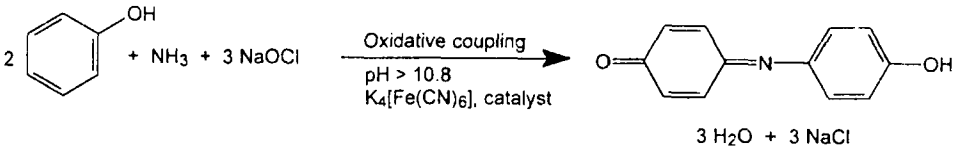


Figure 3 Reconstructed linear regression analysis plot for enzymatic method results vs. automated alkali-phenate to indophenol method: correlation coefficient (R^2), 0.99998; intercept (b) at -34.12 $\mu g.L^{-1}$; and slope (a), 0.9509. Logarithmic scale is used to discern the analytical data points and precision.

detection at 630 nm. The analytical reaction involves the oxidative coupling of phenol with NH_3 in strongly alkaline solution to generate the indo-phenol (blue color) as shown in the scheme 3.

Scheme 3 Oxidative coupling reaction of phenol with ammonia to generate indophenol blue.



However, phenol is strongly acidic and corrosive. A toxic o-chlorophenol is generated by the reaction of phenate in hypochlorite/chlorine solution, under the analytical reaction conditions. Both phenol and o-chlorophenol pose safety and human health concerns[9,25]. In addition, the estimated concentration of NH_3 by the APIP method may be deceitfully high, due to the generation of additional NH_3 from the hydrolysis of interfering species such as primary amines, amino acids, urea, allantoin or other ammonia generating particulates in alkaline solutions.

Analytical precision for the enzymatic method was estimated and compared against the APIP method and the results are presented in Table 2. Low precision of the results from the enzymatic method is directly related to the ambient reaction conditions against the automated analysis employed for the APIP method. The precision for the enzymatic method could be improved by temperature control, automated delivery of the analytical reagents and analytes and precise timing of the analytical reaction. Under the current analytical conditions and with minimum enzyme concentration (9.5×10^3 $U.L^{-1}$), accurate results were obtained with 3 replicate measurements which required less than 1.0 mL total sample volume. Comparatively, the APIP method required 9.0 mL total sample volume for triplicate analysis. However, the estimated impinger solution volume after 6 hours sampling period was less than 5.0 mL in the first impingers. Therefore, the enzymatic method is more suitable for micro-environmental sampling devices which require minimum sampling time and extraction volume.

Ammonia concentration in swine farming environment

Air samples were collected at the breathing zone of farm workers in the swine farming. The estimated concentration of ammonia inside the swine confinement facilities and outside of the swine farming facilities for the period from July 1995 to October 1995 is reconstructed in Figure 4. During the period from July to October, 1995, the observed concentration of NH_3 outside the swine confinement was 210 ± 90 (66 to 330) ppbv. A gradual increase of the concentration of ammonia in the vicinity of the swine confinement facility was observed from summer to fall season (66 ppbv in July, 1995 and 247 ppbv in October, 1995). The indoor ammonia concentration was 1,455 ± 520 (1000 to 2426) ppbv, during the summer to fall season (July—October, 1995). The lowest concentration in indoors was 1,000 ppbv in July, 1995 and the highest concentration was 2,426 ppbv in October, 1995. The highest indoor NH_3 concentrations typically occur during the fall to winter season (April, 1995, 7,000 ppbv; November, 1995, 10,000 ppbv) due to intensive swine confinement. Comparatively, NH_3 concentrations in the urban atmosphere ranges from 1 to 5 ppbv[26,27]. These observations show that the ammonia concentrations in the breathing zone of the swine farm

Table 2 Accuracy and precision data for the airborne ammonia samples from the swine farming environment.

Sample ID method	*Sampling data*	*Enzyme method*	*Alkali-phenate*
		95% confidence level, Mean ± $(t.\sigma).n^{-1/2}$	
Ammonia as NH_3			
PS010496–01B Indoor swine confinement	11–18–95 (Composite)	68.88 ± 38.81 µg/L	70.28 ± 6.96 µg/L
PS010496–02A Indoor swine confinement	11–18–95 (Composite)	94.256 ± 5.19 µg/L	99.13 ± 6.39 µg/L
PS010496–03B Outdoor swine free-control farm	10–17–95 (Composite)	73.4 ± 51.54 µg/L	70.03 ± 11.73 µg/L
PS010496–04A Outdoor swine free-control farm	10–17–95 (Composite)	364.1 ± 29.79 µg/L	323.81 ± 0.57 µg/L
PS010496–05B Outdoor swine confinement	10–12–95 (Composite)	68.88 ± 20.09 µg/L	79.74 ± 3.81 µg/L
PS010496–06A Outdoor swine confinement	10–12–95 (Composite)	10.06 ±1.16 µg/L	10.90 ± 0.12 µg/L
PS010496–07 Blank	11–18–95 (Composite)	75.19 ± 16.16 µg/L	90.49 ± 7.60 µg/L
PS010496–08 Blank	10–17–95 (Composite)	88.22 ± 30.74 µg/L	46.96 ± 3.81 µg/L
PS010496–08 Blank	(Composite, Impinger A and B)	3.53[a] ± 24.97 µg/L	90.49 ± 7.60 µg/L
Phosphate-citrate buffer		9.12 ± 37.53 µg/L	
Amout utilized per test Limit of detection (3 s.d.)		0.2 mL 107 ± 2.65 µg/L	3.0 mL 16 ± 5.0 µg/L

a. Extrapolated value

environment (both inside the swine confinement facilities and in the vicinity of the swine confinement facilities) are higher in late fall through early spring than in the summer. It is significant to note that the mean comfort temperature in the 'managed confinement facilities' will vary no more than 5°C (22°C in the farrowing units and 18°C in the finishing units) during the 6 hours of sampling period. In contrast, the outside temperature is very much dependent upon the seasonal or climatic variations. In this study, during the six hours of outdoor sampling in the vicinity of swine confinement facilities, temperature variations of up to 12°C were observed. The rate of volatilization of NH_3 is directly related to temperature, and the rate will approximately double for every 10°C increase in temperature. Therefore, the estimation of time-weighted concentration of ammonia requires time integrated temperature corrections. In the breathing zone, polar chemical species such as urea, amino acids, allantoin, uric acid and or biological residues are unlikely to be present as a gas or vapor by the volatilization process, but may be present as aerosols. In Yokohama, Japan, an industrial metropolis,

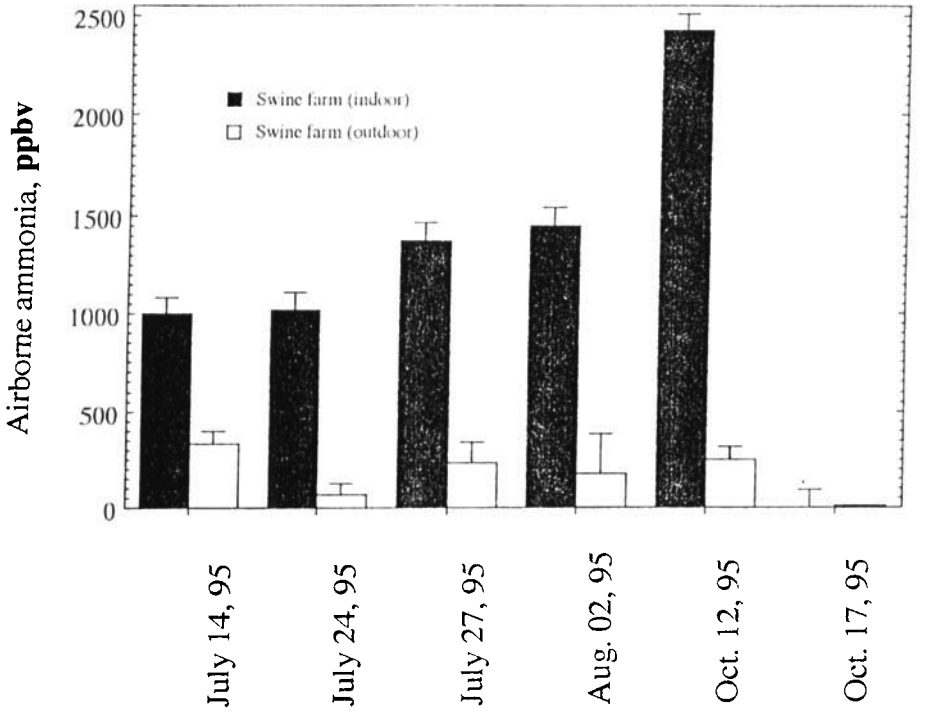


Figure 4 Ammonia concentration inside the swine confinement facility and outside the swine confinement facility during the period from July 95 to October 95. The ammonia concentration result shown for the October 17, 95 is from a swine-free animal house.

ca. 11.3 ± 4 ppbv ammonia level has been measured between January 1987 to December 1991 at 14 m above ground[28]. At this sampling height, NH_3 concentration is high during the summer period peaking to 10 ppbv and in the winter months below 5 ppbv. Even though Yamamoto and coworkers[28] have observed the clear correlation between the humidity and ammonia concentration in the atmosphere, we are unable to notice any significant correlation between humidity and concentration of ammonia in the breathing zone of the swine farming environment.

SUMMARY

In summary, the estimated concentration of NH_3 outside swine farming operations is at least 10 to 20 times higher than the average ammonia levels reported in the urban and industrial metropolitan atmosphere. Ammonia concentration within the swine confinement facility is 250 to 750 times higher in the summer and greater than 1,500-fold in the fall and spring seasons compared to atmospheric NH_3 concentrations. The fluorimetric enzyme method is suitable for the analysis of the aerosolized ammonia in the swine farming environment. The analytical results from this study suggest the enzyme method is specific for ammonia or ammonium ion only and ammonia generating particulates do not interfere. The enzymatic method also effectively eliminates the possibility of falsely elevated results for ammonia which may arise from the use of other alternate analytical methods.

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