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Potential use of gas sensors in beef manure nutrient content estimations

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The purpose of this study was to develop a gas sensor array to estimate the manure nutrient contents. Three metal-oxide gas sensors including methane, ammonia and hydrogen sulfide were used. Forty manure samples were collected from four beef operations in Southwest North Dakota. Manure samples were sent to be analyzed for moisture content, total-nitrogen (Total-N), phosphorus (P), potassium (K) and ammonium-nitrogen (NH_4-N). Regression equations were developed showing the relationships between sensor array readings and the lab results. The sensor array was able to estimate manure N, P, and K with correlation coefficients of 0.80, 0.76 and 0.70, respectively.

Key words: Waste management, animal manure, crop nutrient, gas sensors.

INTRODUCTION

Livestock production is a major industry in North Dakota. Manure produced by about 1.75 million cattle and 150,000 swine in North Dakota may results in serious water quality impacts in many areas (Johnson, 2005). Large land areas, high crop production and low population densities are the advantages of North Dakota in regards to potential problems from manure handling. However, excessive manure application rates or applying manure at the wrong time or place will result in water pollution.

The goal of a successful manure management based on land application is to maximize crop production while minimizing pollution potential. This requires knowledge of the manure characteristics. Manure characteristics have been found to be quite variable (Lindley and Johnson,

1987). Collecting representative samples and getting timely analysis is critical.

Data on manure characteristics can be obtained in three ways: literature values, laboratory analysis of manure and quick tests. Because each manure pile or pit has different characteristics, the literature values are approximated and variations are expected. Even small deviations can result in significant differences because so many thousand pounds or gallons of manure are applied to the field (Kessel et al., 1999).

Manure nutrient values are often based on information from various standard literatures. However, season, management, storage method and other factors may influence nutrient content. Collins et al. (1995) reported that using tabular estimates is not as reliable as regular manure testing for manure management planning.

The accurate way to determine manure characteristics is to have sample analyzed by a laboratory, but generally it takes two to three weeks, and costs $35 to $100 per sample. However, producers want to know the application rate at spreading time instead of waiting two or three weeks to receive the results (Dagnew et al., 2000).

There are some quick tests available in the estimation of manure nutrient contents including hydrometer, conductivity meter, conductivity pen, ammonia electrode, reflectometer, Agros N Meter, Quantofix-N volumeter

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Abbreviations: A, Total area under the curve (Vs); **a, b, c, d**, regression coefficient; **e**, intercept; **H_2O**, manure moisture content (%); **t**, time (s); **Vb**, baseline corrected sensor voltage at a given second i, volt; **Vi**, sensor voltage at a given second i, volt; **Vmin,** minimum sensor voltage obtained during the operation, volt and **y**, nutrient concentration (%).

(Kessel et al., 1999).

Kessel et al. (1999) reported that the quick tests were more effective with slurries than solid manures. Ammonia electrode's fragility and difficulty of setting it up limits the suitability for on-farm use. Nitrogen meter requires use of chemical reagents and cleaning of the meter needs extra attention. All these quick tests provide data for a specific constituent or a certain type of manure. Another signifi-cant disadvantage of the quick tests is that they sense only ammonia, which is not a consistent percentage of total nitrogen. Depending on the manure type, ammonia-nitrogen (NH_3-N) can be 8, 67, and 80% for solid manure, pit manure and lagoon effluent, respect-tively (Millmier et al., 2000; Lorimor, 1999).

With recent advances in technology and electronics the sensory measurement and characterization of properties of organic products is becoming a reality (Ouellette, 1999). Millmier et al. (2000) evaluated the effectiveness of near-infrared (NIR) for quickly analyzing the manure nutrient contents. They were able to identify NH_3-N, P and K with correlation coefficients of 0.69 to 0.98.

There has been a great deal of research effort related to sensor applications. Balasubramanian et al. (2005) used a commercially available e-nose that employs 32 conducting polymer sensors to identify spoilage of beef. Their study indicated that e-nose is capable of classifying stored beef into two classes (spoiled and unspoiled).

Younts et al. (2005) used a gas sensor array to detect and differentiate between different species of bacteria. They concluded that based on the ability to detect dif-ferences in the gas patterns, gas sensors can be used to differentiate *Escherichia coli* 0157:H7 from Non-0157:H7.

Machado et al. (2005) used Cyranose e-nose system to detect lung cancer in human. They tested the system in 59 volunteers (14 lung cancer patients, 25 people with other lung disorders and 20 healthy people). Results showed that e-nose was able to detect those with lung cancer by smelling the breath of the patients.

Dodd et al. (2005) used an electronic nose containing 16 tin metal oxide sensors with various sensitivities to classify decay times of tilapia (*Oreochromis niloticus*). They achieved a classification accuracy of 78.8% for least squares and 83.8% for K-nearest neighbor.

Since odorous compounds result from decomposition of manure, which is achieved by a mixed population of bacteria, amount and type of odorous gases depend on amount and type of bacterial activity (Sheffield and Bottcher, 2000). Hence, by knowing the gas generation pattern of manure samples it could be possible to esti-mate manure nutrient contents. The major gases produc-ed by the bacterial activity are methane, ammonia and hydrogen sulfide.

Therefore, objective of this study was to determine whether metal-oxide gas sensors could be used to quick-ly estimate manure total nitrogen (N), phosphorus (P), potassium (K) and ammonium nitrogen (NH_4-N) in beef feedlot manure.

MATERIALS AND METHODS

Operation mechanism of metal-oxide gas sensors

The sensors used in this study were TGS-842, TGS-825, and TGS-2602 (Figaro USA, Inc., Glenview, Ill.) that are sensitive to methane, hydrogen sulfide, ammonia and hydrogen sulfide, respec-tively.

The metal-oxide sensor is a thick film detector made by coating a film of tin oxide sintered on a small ceramic tube (Bartlett and Gardner, 1992; Ho et al., 2001). When the sensor is exposed to an atmo-sphere containing reducing gases, such as ammonia, methane, etc, the tin-dioxide surface adsorbs these gas molecules and these gas molecules cause oxidation. A simple electrical circuit can convert the change in conductivity to an output signal, voltage.

A sensor array was assembled for collecting, monitoring and recording headspace gas generations from manure samples. An array consisting of four sections including sample, and three sensor compartments was built (Figure 1). Interconnections between the sensor array and signal circuits and circuits and data acquisition board were assembled. Sensor types, target gases, and their sensitivities are listed in Table 1. A data acquisition board (Dataq Instruments Inc., Akron, Ohio) was used to acquire and transfer signals from circuits to the computer. A simple program using UltimaSerial ActiveX control was written in Microsoft Excel to acquire record and plot real-time signals from data acquisition board.

Three single-head, micro diaphragm pumps (Hargraves Tech. Corp., Mooresville, N. C.) were used to purge manure headspace gas from sample compartment to sensor compartments. A 12 Volt, 50 x 50 mm computer cooling fan was used to circulate manure headspace gas in the sample compartment. Three 12 Volt, 76 x 76 mm computer coolers were used as exhaust fans to remove the manure headspace gases after the operation.

Sample preparation and acquiring headspace gas data

Forty fresh manure samples were collected from four South-western North Dakota beef operations in summer of 2006. Samples were collected in the morning time for one week. All the cattle were being fed oat, alfalfa, or mixed hays. A 550 W food processor was used to homogenize the samples. Two portions of each manure samples weighing approximately 400 g were poured into a 10 x 19 cm Ziploc® bag and frozen until the time of analysis. One portion was stored to collect headspace gas generation data and other corresponding portion was sent to the North Dakota State University Soil Science Department laboratory to be analyzed for Total-N, P, K, and NH_4-N as described in Peters et al. (2003).

A sample container having 55 ml of volume with 6 cm top opening was used to collect responses of gas sensors to the headspace of manure samples. Prior to surging the sensor array with headspace gas, all exhaust and mixing fans and pumps were operated to remove any unnecessary moisture and odor from the system for two minutes. Before running a sample, all exhaust openings were closed and all pumps and fans were switched off. After placing the sample and closing the lid, mixing fan in sample compartment and surging pumps were started simultaneously. To avoid the cooling effect of mixing fan on the sensors, it was switched off after 10 s. Gas measurement, expressed in volts, was plotted for four minutes at a sample rate of 1 reading/s, generating a gas signature. After each run, all exhaust fans and pumps were operated to remove headspace gas. The above protocol was a
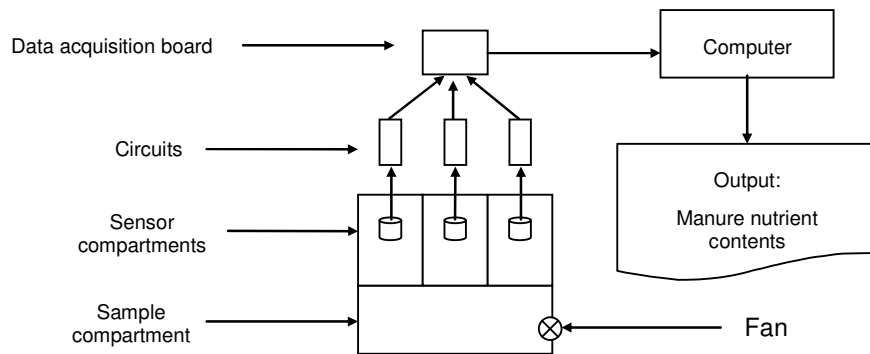
Figure 1. Schematic representation of the gas sensor array.

Table 1. Sensors used in the array, their target gases, and the sensitivities.

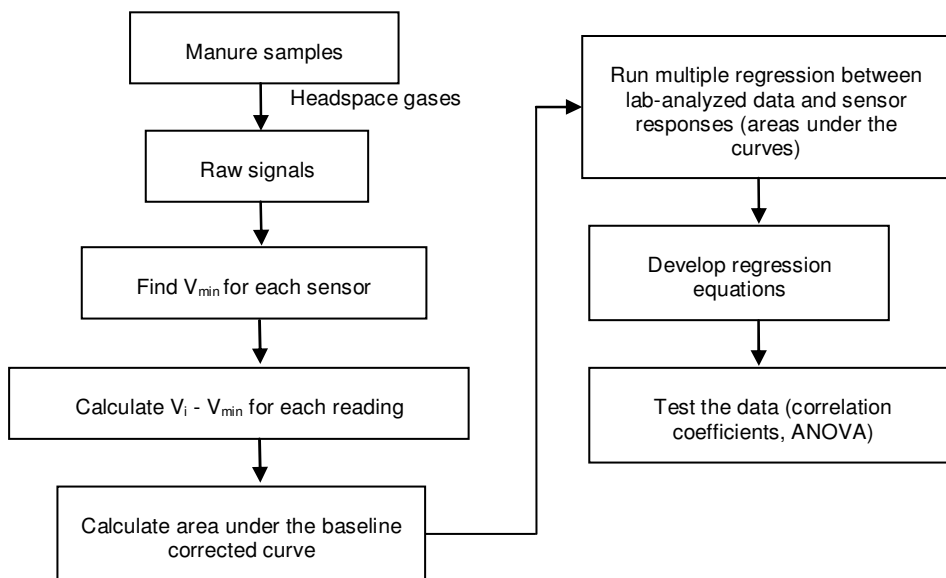| Sensor	Target gas	Sensitivity (mg/l)	Price ($)
TGS-842	Methane	500-10000	15
TGS-825	Hydrogen sulfide	5-100	56
TGS-2602	Ammonia and hydrogen sulfide	<10	56

Figure 2. Steps in data collection and processing.

result of experiments to identify the optimum sampling time and sample amount.

Data processing

All steps in data collection and processing used for developing regression equations are shown in Figure 2. Since there werenot major fluctuations in raw sensor voltage data, no smoothing techniques was applied. Raw sensor data were baseline-corrected using the following equation.

$$V_b = V_i - V_{min}$$

(1)

Where V_b = baseline corrected sensor voltage at a given second i, V_i = sensor voltage at a given second i, V_{min}: is minimum sensor voltage obtained during the operation.
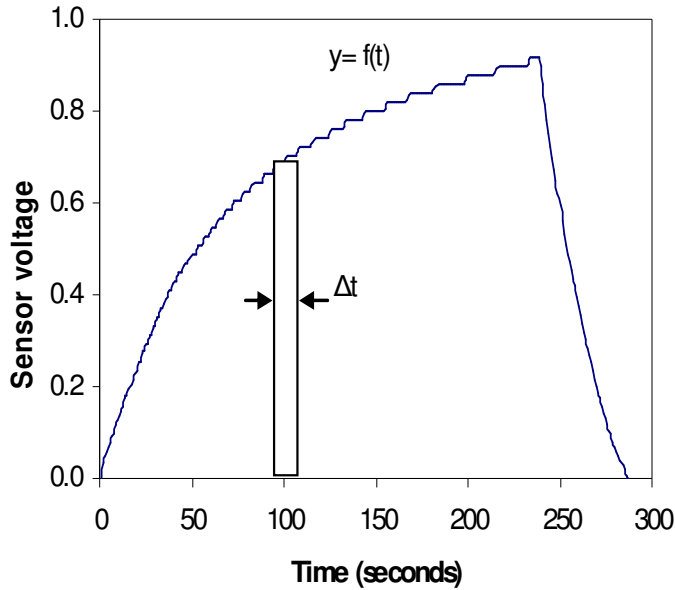
RESULTS

The gas signatures from three sensors, and manure moisture contents were used as variables to develop regression equations. The best prediction model for each nutrient content was determined by observing the highest r value, lowest SE and number of variables. It was aimed to select models with fewer variables. However, multiple regression analysis for calibration models showed that there is a good correlation among all sensor readings (variables), manure moisture and nutrient contents (Table 2). Except NH_4-N other nutrient compounds could be estimated with a high correlation coefficient and a low SE using all variables. Manure NH_4-N concentrations varies in a range of 66 – 447 mg/l, and only the methane sensor is capable of sensing in this range. Therefore an insignificant correlation was observed for NH_4-N, as anticipated.

The predictor variables and their regression coefficients can be expressed as:

$$y = aA_M + bA_H + cA_A + d(H_2O) + e \qquad (3)$$

Where y = nutrient concentration (%), a, b, c, d = regression coefficients, e = intercept, A = area under the baseline corrected senor response curve (Vs), H_2O = manure moisture content (%), and M, H, A = denoting methane, hydrogen sulfide and ammonia sensors, respectively.

Rewriting equation 3, based on equation 2, yields:

$$y = a\left(\sum_{k=1}^{240} f(t_k)_M \Delta t_M\right) + b\left(\sum_{k=1}^{240} f(t_k)_H \Delta t_H\right) + c\left(\sum_{k=1}^{240} f(t_k)_A \Delta t_A\right) + d(H_2O) + e \qquad (4)$$

Regression coefficients for the prediction equations of manure nutrient contents are given in Table 3. In order to see if the predictor variables in regression analysis are good fit in determining the response variables, ANOVA was used. The results of ANOVA for a 95% confidence interval are presented in Table 4.

$$F > F_{[\alpha]}^{(v-1,n-v)} = F_{[0.05]}^{(4,24)} \text{, and } P-value < \alpha = 0.05$$

Larger F values were obtained in comparison to F-critical values associated with smaller P-values for Total-N, P and K predictions. This concludes that statistically significant differences exist among the predictor variables, and they are a good fit in determining the manure Total-N, P and K contents. However, a smaller F value in comparison to F-critical, and a larger P-value than 0.05 were obtained for NH_4-N prediction. Therefore, NH_4-N prediction equation cannot be used. In order to validate the calibration models, other 10 samples were used. R^2 values between predicted and observed nutrient contents

Figure 3. Baseline corrected sensor response curve.

Table 2. Regression statistics for prediction equations.

Parameter	Total-N	P	K	NH₄-N
r	0.75	0.60	0.90	0.32
Standard error	0.05	0.05	0.04	104

A typical baseline corrected sensor response curve is shown in Figure 3. In the calculation of the areas under the curves it is assumed that the sum of all the rectangles will be approximately equal to the area under the curve (equation 2). Therefore,

$$A = \sum_{k=1}^{240} f(t_k)\Delta t \qquad (2)$$

where A= total area under the curve, t = time (s), k = designation number of each rectangle, Δt = Vs, and V = sensor voltage.

Three areas corresponding to three sensors were extracted for each manure sample. Since there is little consensus on the most appropriate method, multiple regression was used to develop prediction models. Thirty manure samples were used to develop calibration models. Microsoft Excel's data analysis tool was used to conduct multiple regression analysis. Multiple regression, equations were developed for total-N, P, K, and NH_4-N predictions. Higher correlation coefficient (r) and lower standard error (SE) were considered to select the superior model. Higher number of variable may increase the r value. However, adding an unimportant variable may increase the SE as well. Therefore, in the selection of best prediction model, different number of variables and their effects on r and SE values were observed. Analysis of variance (ANOVA) was used to test the quality of the predictor variables. Finally, calibration models were tested using the other 10 samples. R^2 values between predicted and observed manure nutrient contents determined to test the quality of the calibration models.

Table 3. Coefficients for regression equations.

Regression coefficient	Manure nutrients		
	Total-N	P	K
a	0.00165	-0.00037	-0.00279
b	0.00036	0.00065	0.00180
c	-0.00015	-0.00011	-0.00041
d	-0.02466	-0.00874	-0.01824
E	2.46476	0.76785	1.67024

Table 4. ANOVA results.

Manure nutrients	F-value	P-value	F-critical
Total-N	7.63	0.00041	2.78
P	3.41	0.02430	2.78
K	25.96	2×10^{-8}	278
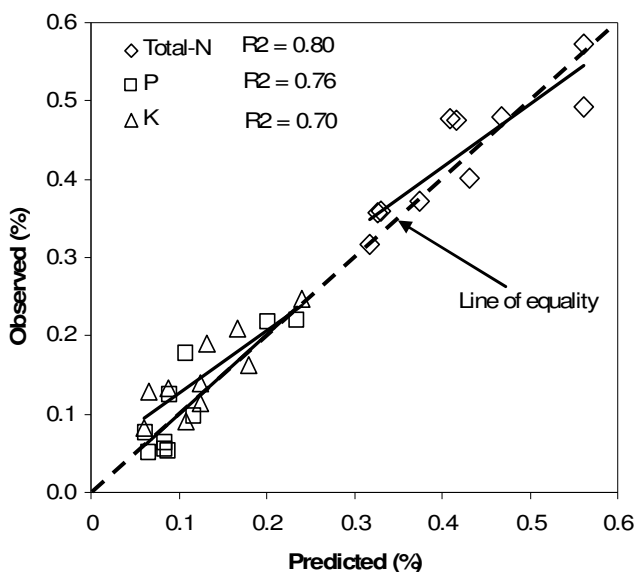
Figure 4. Relationship between predicted and observed manure nutrient contents.

are given in Figure 4. Higher R^2 values indicate that regression models can be used to estimate manure nutrient contents.

The data from this study show that metal-oxide gas sensors could be used as a tool for indirect estimations of manure nutrient contents. However the linear regressions obtained in this study cannot be used for all animal species. Zhu et al. (2003) reported that the best approach for indirect estimations of manure nutrient contents is to develop separate regression equations for manure from the animals that are receiving similar feed ratios.

DISCUSSION

A sensor array consisting of three metal-oxide gas sensors were used to estimate beef manure Total-N, P, K and NH_4-N contents. A data acquisition board was used to acquire the raw sensor signals. The signals acquired at a sampling rate of 1 reading/s was plotted to calculate the area under the curve that will be used as a predictor variable.

Sensor responses and actual manure contents were used to develop linear prediction equations. Higher correlation coefficients of 0.80, 0.76, and 0.70 for Total-N, P, and K, respectively, were obtained. The ANOVA tests also confirmed that the predictor variables, gas sensor responses and manure moisture content, are good fit in determining the manure Total-N, P, and K contents.

This preliminary study also indicated that sensor and computer technology can be used as tool for better management of animal manure. Our future work involves the development of a hand-held device that will employ different and more precise sensors to improve the accuracy of the system with other animal species.

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