RESEARCHREPORT
ENVIRONMENT

Title: Application of Near-Infrared Technology to Swine Manure Analysis
NPB# 98-243

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Abstract

Ninety seven samples were obtained from swine finishing manure pits. The samples were used to test and compare two NIR machines for prediction capabilities of manure nutrients. An NIRSystems 6500 provided good predictions of total solids and phosphorus, and fair predictions of total Kjeldahl nitrogen and ammonia. A Bruker machine provided poor predictions for the liquid manure samples. Different machines will have to be individually calibrated and evaluated to be used for NIR predictions of manure nutrients.

Nutrient concentrations were examined. In general nitrogen and phosphorus concentrations were lower than current state estimates. TKN averaged 39.5 and P_2O_5 32.6 lb/1000 gal, respectively. Ammonia constituted nearly 80% of the total nitrogen in the samples.

Statistical methods were used to define the accuracy of predictions based on the number of buildings sampled. For a single sample from a single building nitrogen can be estimated to within + 7.5, and P_2O_5 to within 10.7 lb/1000 gal. respectively.

Introduction

This project was a continuation of an initial project funded by the Multi-state Consortium on Animal Wastes to develop Near infrared (NIR) technology to rapidly determine nutrient concentrations in animal manure. The project was to further the work towards developing NIR technology to quickly test manure for nutrient concentrations. Rapid testing will enable producers to do a much better job of manure application to optimize crop production, minimize costs, and minimize environmental risks.

This final report covers work done under contract with the National Pork Producers Council for the period from November 13, 1998, until October 31, 1999. The NIR work was done in the ISU Food Science Building in Dr. Charles Hurburgh's NIR grain laboratory.

Objectives

This project had two primary objectives:

1. Field test previously developed calibrations, and compare two different NIR instruments.
2. Use the samples collected for the NIR testing to update current manure nutrient estimates.

Methods and Procedures

A total of 97 liquid swine pit manure samples were collected from 25 separate houses located at eight multi-building sites. These samples were collected in addition to the 141 samples that had been previously collected. All of the new samples except nine were from finishing deep pit houses. Nine samples were from a nursery. Samples were collected from multi-building sites in order to allow examination of house-to-house, and farm-to-farm variation. All samples were obtained by the same person using uniform sampling techniques. Samples were drawn from the top, middle, and bottom of the pits using a sampling tube with a valve on the bottom. A vertical profile sample was also obtained from each pit. The samples were frozen until tested.

Agribusiness systems in Iowa (and one in Missouri) were questioned to locate a NIRSystems 6500 instrument so that a comparison could be made between their (slave) instrument and the "master" unit on campus that was used for the initial NIR project. No NIRSystems 6500's could be located, so the decision was made to compare two different types of NIR Instruments, the NIRSystems 6500, and a Bruker.

For testing, the samples were thawed overnight and allowed to come to room temperature. Once thawed they were shaken by hand, and approximately 70-80 ml of each sample were poured into an 8-cm by 15-cm, 6-mil Ziploc® bag. The temperature of each sample was determined just prior to scanning using a C-1600P TherMonitor manufactured by Linear Laboratories. Temperatures averaged 25.5^{O} C with a standard deviation of 0.55^{O} C. The temperature range was from 23 to 27^{O} C. The samples (contained in the Ziploc® bags) were individually scanned in the two machines. They were sent to Dr. Wendy Power's wet chemistry laboratory in the National Swine Research and Information Center at Iowa State University for chemical analysis. They were analysed for total solids, volatile solids, total Kjeldahl nitrogen, ammonia nitrogen, phosphorus, and potassium. The nutrients of primary concern were total Kjeldahl nitrogen, ammonia nitrogen, and phosphorus.

Comment:

Results

Initial calibrations were developed for the NIRSystems 6500 instrument located in Dr. Hurburgh's lab at ISU. Figure 1 shows selected scans to illustrate the type of output provided by NIR instruments for swine pit nutrient analysis with varying solids contents.

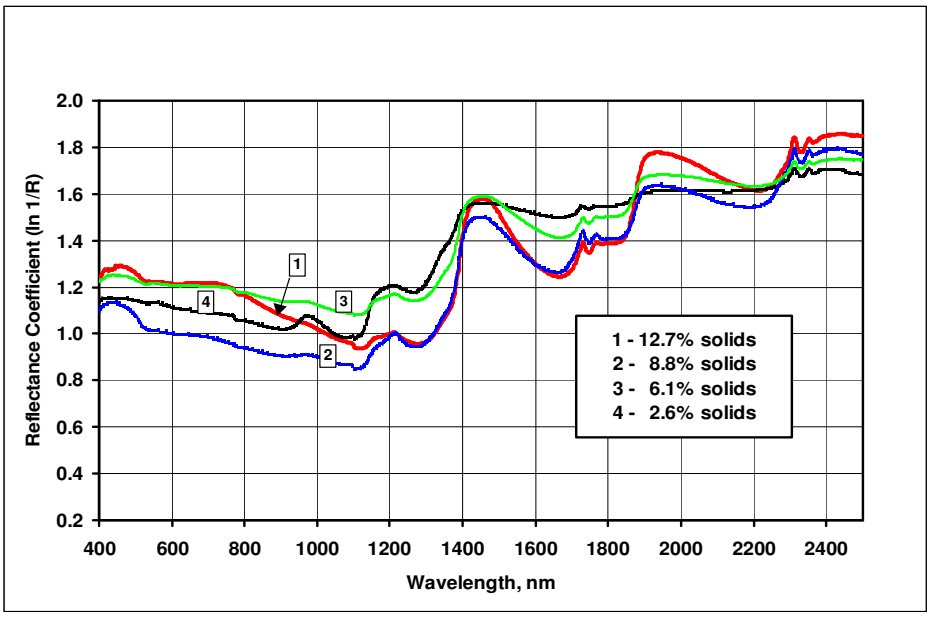

Figure 1. Scans of swine pit samples containing varying solids concentrations.

Calibrations were derived for each constituent by using a PLS Regression techniques using WINISI II for the 6500 and The Unscrambler® data analysis software for the Bruker (The Unscrambler® 6.11a, Camo A/S, Oslo, Norway, 1997). PLS regression is a bilinear modeling method that relates the variation in each response variable (Y-variable) to the variations of several predictors (X-variables). PCA was used to eliminate outliers. PCA projects the information carried by the original variables onto a smaller number of underlying ("latent") or orthogonal variables called principal components. After scanning all samples, calibrations were developed between the reflectance patterns across the wavelength spectrum for each individual chemical constituent for each machine using grouped data. The best correlations were sometimes found by using only a portion of the spectrum. In those cases the unused portion of the spectrum was truncated. An example is shown in Figure 2.

Once the calibration equations were developed using the grouped data, individual samples could be compared to the predicted values from the calibration equations.

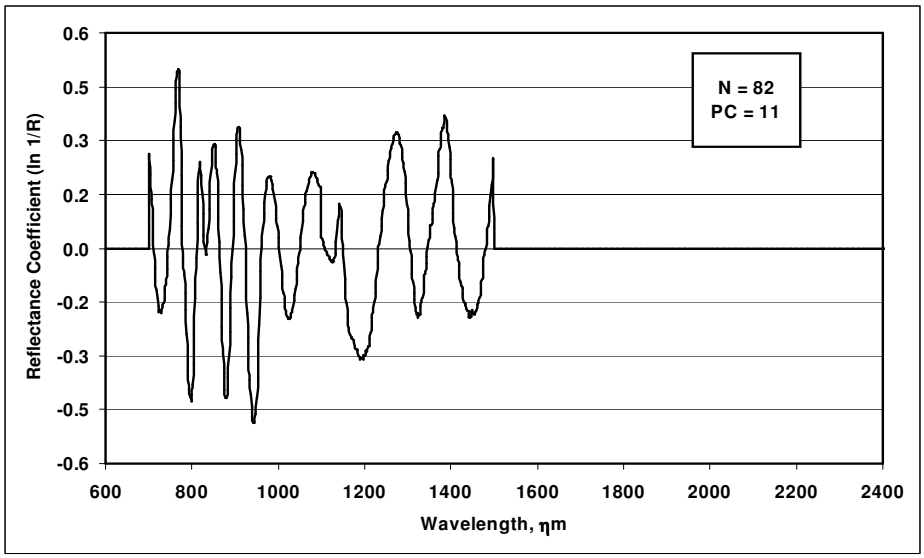

Figure 2. Only a portion of the spectrum (650-1500 ηm) is used for this constituent (total solids) to optimize the correlation with wet chemistry analysis.

Statistical analysis of the data was based primarily on standard error of prediction (SEP), which is normally used in NIR analyses. SEP is a measure of scatter, or dispersion, of the actual nutrient concentrations about the regression line. The smaller the SEP, the closer the estimate is likely to be to the actual value of the dependant variable. The SEP was then used to calculate the ratio of range:SEP for each nutrient for each machine. The range was the difference between the high and low nutrient concentrations. Since a small SEP indicates the likelihood of good estimates, a large range:SEP indicates accurate predictions can be expected over a large data range. A ratio of range:SEP between 4 and 8 indicates only a possibility of distinguishing between high and low values (poor predictability). With a range:SEP between 8 and 12, there is a possibility of predicting quantitative data (fair predictibility). A ratio of range:SEP greater than 12 indicates good predictability (Williams and Hurburgh, 1999). The statistical analysis is summarized in the Table 1.

Table 1. Calibrations for total solids, total Kjeldahl nitrogen, ammonia nitrogen and phosphorus in swine pit manure using NIRsysems 6500 and Bruker machines.

Statistic		Constituent							
		TS[a]		TKN[b]		NH3-N[b]		P[b]	
		NIR 6500	Bruker	NIR 6500	Bruker	NIR 6500	Bruker	NIR 6500	Bruker
No. of PLS factors		5	9	5	6	6	9	5	8
Correlation,R		0.94	0.748	0.87	0.64	0.85	0.63	0.90	0.67
Correl. Coeff.,r^2		0.89	0.60	0.76	0.41	0.72 4	0.40	0.81 7	0.45
SEP[c]		1.25	2.63	2.39	3.39	2.33	3.32	0.40 2	0.67
Range:SEP		15.8 9	7.55	10.1 5	7.16	9.18	6.44	12.7 6	7.66
Outliers Removed, %		6.2	7.2	10.3	8.2	10.3	10.3	8.2	4.1
Wet Chemistry:									
Dry Basis (% dw)	Mean	5.18		11.49		9.38		3.02	
	Max	20.91[d]		26.67		23.93		6.35	
	Min	1.05		2.41		2.55		1.22	
	SDev	4.20		4.82		4.46		1.03	
Wet Basis (lb/Kgal)	Mean	548.94		39.45		28.40		14.36	
	Max	1426.58[d]		343.19		57.01		58.85	
	Min	236.88		10.42		9.48		1.28	
	SDev	391.47		33.74		8.93		13.56	

Notation: [a] % wet basis
[b] % of dry solids
[c] Standard Error of Prediction
[d] Sticky solids (not liquid) in only one bottom sample

The NIRSystems 6500 predicted nutrients better than the Bruker. As Table 1 shows, the correlation coefficients were higher, and the SEPs were lower. The 6500 results exhibit good predictability for total solids and phosphorus (range:SEP $\geq$ 12), and moderate predictability for TKN and ammonia (8 $\leq$ range:SEP < 12). The range:SEP values for the Bruker were all less than 8, indicating poor predictability for all 4 nutrients.

When predicted nutrient concentrations are plotted against actual values, the two machines produce nearly identical plots indicating that the average predictions for both agree with the wet chemistry values, but the variability is greater for the Bruker as shown in Figures 3 through 6. Thus Bruker prediction errors are likely to be greater than predictions by the 6500. The Bruker data points tend to lie outside of the 6500 data points on the plots.

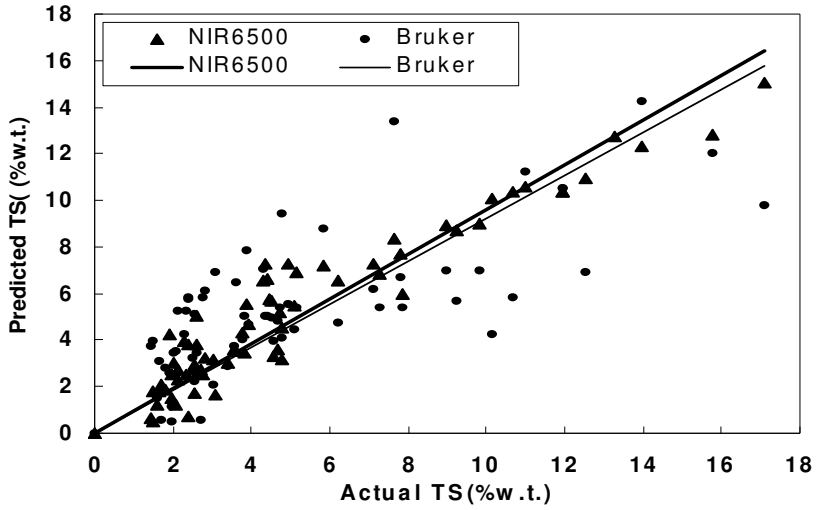

Figure 4. Predicted versus actual concentrations for total Kjeldahl-N using two NIR machines, R^2 is 0.89 for NIRsystem 6500, and 0.44 for Bruker.

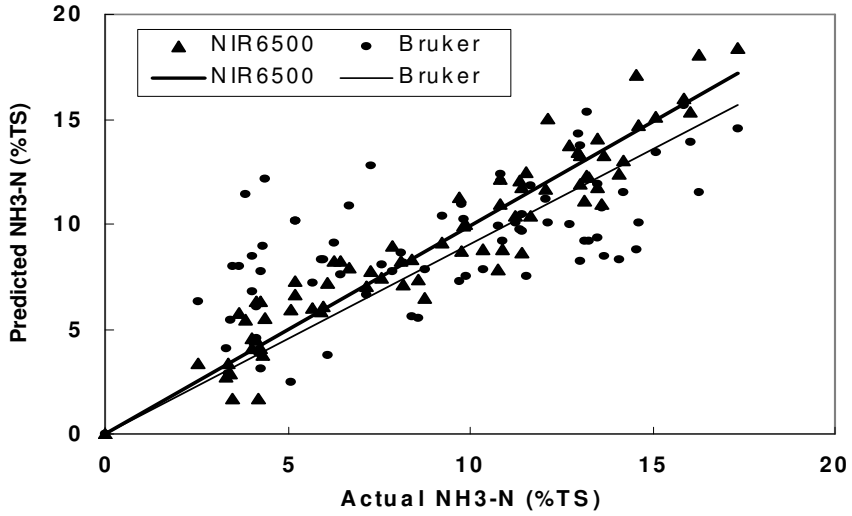

Figure 5. Predicted versus actual concentrations for ammonium-N using two NIR machines, R^2 is 0.89 for NIRsystem 6500, and 0.39 for Bruker

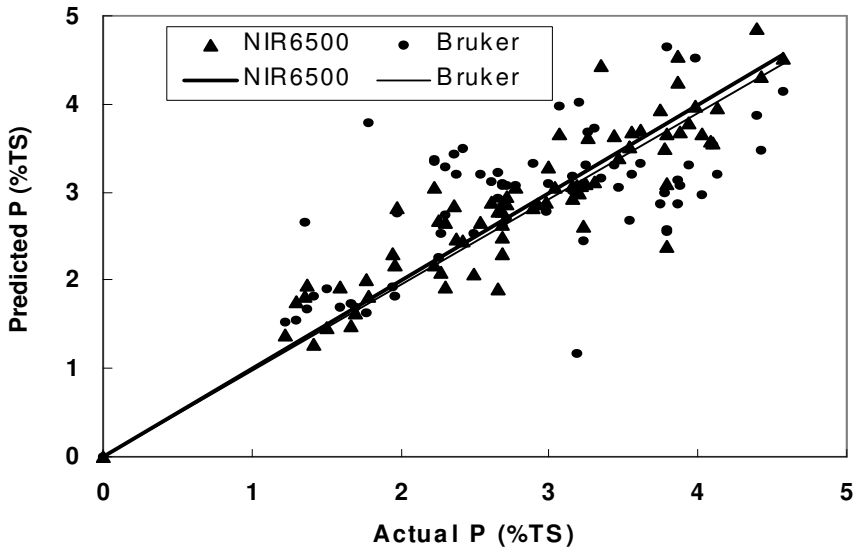

Figure 6. Predicted versus actual concentrations for phosphorus using two NIR machines, R^2 is 0.81 for NIRsystem 6500, and 0.42 for Bruker

The second objective was to examine nutrient concentrations of the samples. As shown in Table 1 above, the mean concentrations for all 97 samples were 39.5 and 14.4 lb/1000 gal. lb/1000 gal. of TKN and P respectively (32.6 lb/1000 gal. expressed as P_2O_5). Current state estimates are 50 and 42 lbs/1000 gal., respectively for swine

finishers with traditional dry feeder systems, so N and P_2O_5 in these samples are 35 and 22% lower than the state estimates, respectively. In Table 1, the standard deviations are almost as large as the average values, but are affected by the top-middle-bottom sampling procedure which increases the variability dramatically. Table 2 shows the sample analysis for vertical profile samples only.

Table 2. Nutrient analysis for vertical profile samples from 25 finishing barns.

	TS	*P*[a]	*TKN*	*NH3-N*
Average	4.0	10.9	33.7	26.8
Maximum	6.5	22.1	52.2	40.4
Minimum	1.0	1.4	12.3	10.6
Std deviation	1.3	4.7	8.2	6.4

[a] to calculate as P_2O_5, multiply by 2.27

Figure 7 shows TKN concentration averages at the top, middle, bottom, and vertical profile for each multiple-building finishing site. In general, TKN concentrations at the top and middle are similar; and the bottom sample is much more concentrated than the other two indicating a uniform nutrient concentrations throughout most of the pit above the settled solids. The vertical profile concentrations fall between the bottom and the other two sample concentrations.

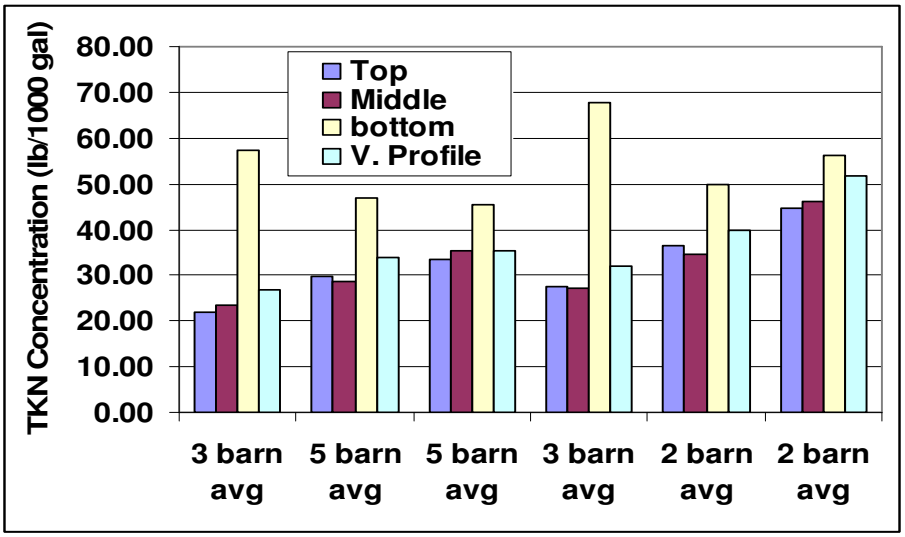

Figure 7. Per-farm average TKN concentrations for top, middle, bottom, and vertical profile samples.

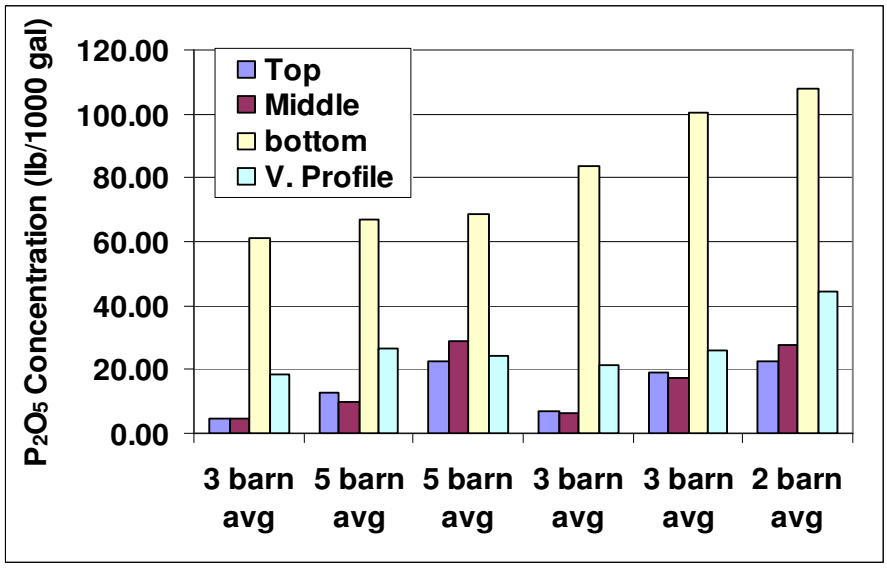

Figure 8. Per-farm average P_2O_5 concentrations for top, middle, bottom, and vertical profile samples.

Nutrient concentrations in the top samples were compared to nutrient concentrations in the vertical profile samples to see if dipping a sample from the top of a pit will provide a reliable estimate of the average concentration throughout the pit. Table 3 shows results of that comparison.

Top concentration / Vertical profile concentration				
	TS	*P*	*TKN*	*NH3-N*
	%	%	%	%
Average	75.21	72.26	90.02	93.41
Maximum	112.78	299.15	123.08	113.67
Minimum	31.35	17.13	70.58	78.49
Std. dev.	24.66	59.77	11.97	9.42

Table 3. Summary of nutrient concentrations in top samples divided by vertical profile nutrient concentrations, n = 23.

A sample dipped from the top does not accurately represent a defined percentage of the vertical profile for TS or P. Top/vertical profile variability, however, is much less for TKN and NH_3-N, with standard deviations of 11.97 and 9.42 lb/1000 gal, respectively. All TKN samples were within $\pm$ 23% of the mean. On the average for the 23 pits examined the TKN concentrations in a sample dipped from the top of a pit will be 90% of the pit average. This results agrees well with sampling done for other projects. Ammonia (immediately plant available) constituted an average of 79.8% of TKN in the vertical profile samples.

Statistical analyses were done to address the question “how many samples should I take to know my nutrient concentration accurately?” Figure 9 and 10 show the results of the analysis.

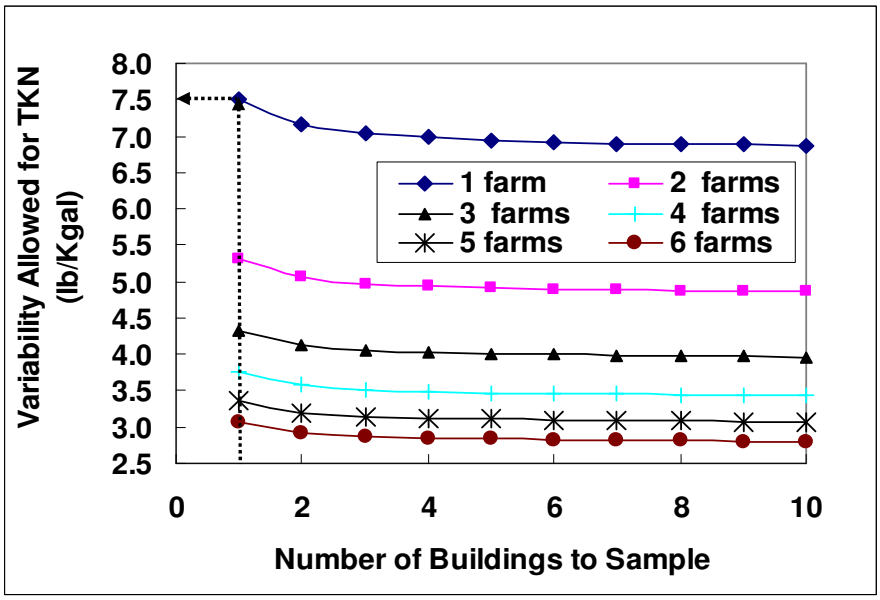

Figure 9. Number of buildings to sample to be within an allowable variability of TKN.

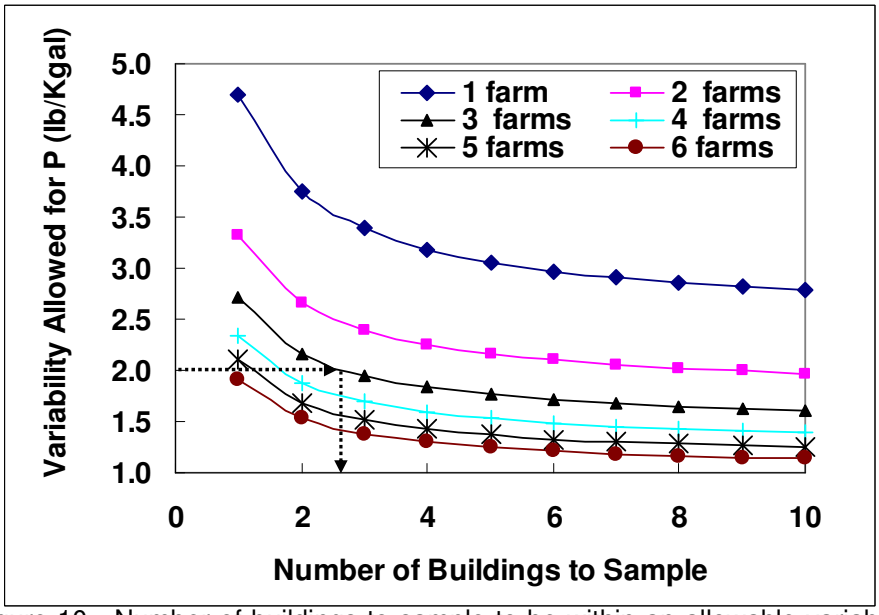

Figure 10. Number of buildings to sample to be within an allowable variability of P_2O_5 concentration.

The following examples are presented to illustrate how to interpret Figures 9 and 10:

EXAMPLE: If I take 1 sample from my single building, how closely can I expect to estimate the TKN?
ANS: From Figure 9, reading vertically upward from one building to the “1 farm” line, then across, you can only be within $\pm$ 7.5 lb1000 gal.

EXAMPLE: I have 5 buildings on each of 3 sites. To know the P with in $\pm$ 2.0 lb/1000 gal. how many buildings should I sample?
ANS: Read across horizontally from the 2.0 lb/1000 gal (on the vertical axis) to the 3 farm line. Then read vertically downward (dotted lines) to see you need to sample 3 out of the 5 buildings on each farm.

Conclusions

Differences exist between the manure prediction capabilities of the NIRSystems 6500 and the Bruker NIR machines. The 6500 did a significantly better job of predicting liquid swine pit manure nutrient concentrations than the Bruker. The 6500 did a good job of predicting TS and P, and a fair job of predicting TKN and NH_3-N. The Bruker did a poor job on all nutrients. Based on these results, NIR methods are not yet ready for testing liquid swine manure nutrients, but the 6500 still appears to have good potential. Clearly each machine to be used for manure nutrient prediction will have to initially be individually tested.

Nutrient concentrations were significant different in top, middle, and bottom samples. Sampling only the top may provide a fair sample of the total pit concentration for nitrogen compounds, but not for phosphorus or solids.

The number of samples necessary to estimate nutrient concentrations at a desired level of precision was investigated. Based on 97 samples, the closest nitrogen can be estimated from sampling one building is $\pm$ 7.5 lb/1000 gal. P can be estimated to within $\pm$ 4.7 lb/1000 gal. (P_2O_5 = 10.7) By sampling additional buildings and/or farms the accuracy of the estimates can be increased.