

# Manure Nutrient Sensing

Application of new techniques: near-infrared (NIR) spectroscopy and nuclear magnetic resonance (NMR) sensor

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## Introduction

Manure is rich in essential elements including nitrogen (N), phosphorus (P), and potassium (K) for plant growth, and thus it is often land applied as an agricultural fertilizer. While utilization of manure is an effective way to restore organic matter and nutrients to the soil, over-application of manure contributes to environmental issues such as eutrophication and water contamination. Manure nutrient prediction and variable rate application are promising new technologies to reduce the risk of over-application by providing real-time manure composition data and are being marketed to Wisconsin dairy farms. One of a widely investigated technology is a near-infrared (NIR) spectroscopy.

NIR has been proven to accurately determine total solid (TS), organic matter (OM), total nitrogen (TN), ammoniacal nitrogen ( $\text{NH}_4\text{-N}$ ) of animal manure in several previous studies. Most of the existing literature investigated spectral data from NIR systems using a reflectance mode, and in this study, both reflectance and transmittance modes were used to develop prediction models for manure composition through a spiking methodology of sample preparation.

A low-field nuclear magnetic resonance (NMR) device is another potential method for predicting manure nutrients accurately. The accuracy and precision of a specific NMR-based manure sensing technique has been assessed for predicting TS,  $\text{NH}_4\text{-N}$ , TN, and P in dairy manure in this study.

## NIR Results

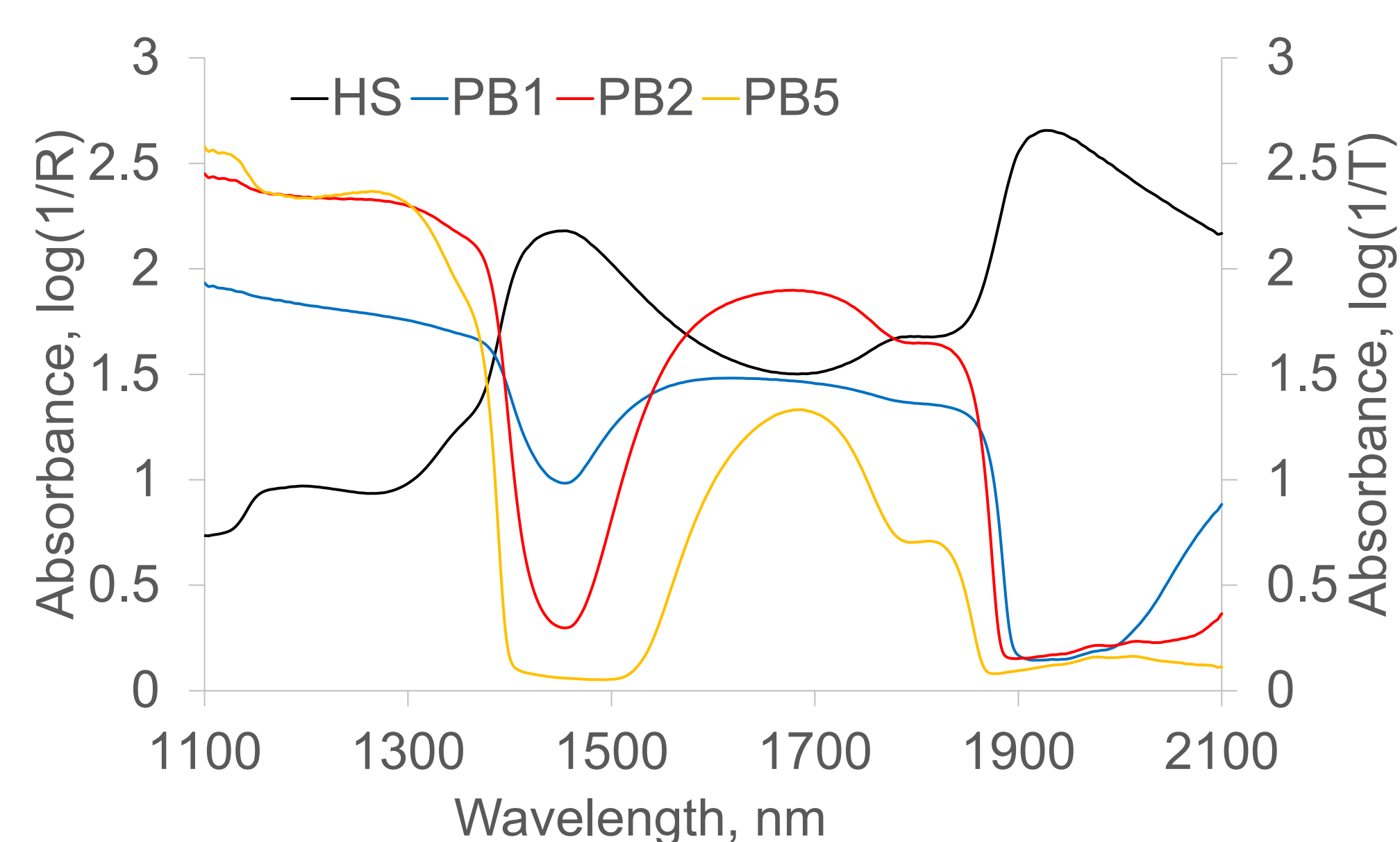


Fig A. Averaged spectrum of 100 samples scanned by reflectance and transmittance sensor configurations.

Table A. NIR calibrations ( $n=100$ ) of manure constituents using reflectance and transmittance sensor configurations based on  $\text{NH}_4\text{-N}$  and Org-N spiking groups.

Config.	$G_{\text{NH}_4\text{-N}}$	LVs	$R^2$	RPD	$G_{\text{Org-N}}$	LVs	$R^2$	RPD
HS	$\text{NH}_4\text{-N}$	7	0.83	2.45	Org-N	12	0.66	1.73
	TS	7	0.90	3.16	TS	9	0.90	3.16
	Ash	7	0.66	1.71	Ash	9	0.72	1.88
	PS	5	0.69	1.79	PS	5	0.67	1.73
PB1	$\text{NH}_4\text{-N}$	9	0.56	1.50	Org-N	6	0.34	1.23
	TS	8	0.97	5.50	TS	6	0.97	5.42
	Ash	7	0.86	2.64	Ash	6	0.87	2.77
PB2	$\text{NH}_4\text{-N}$	1	0.30	1.20	Org-N	8	0.27	1.17
	TS	8	0.88	2.86	TS	8	0.92	3.58
	Ash	8	0.90	3.10	Ash	8	0.88	2.86
PB5	$\text{NH}_4\text{-N}$	1	0.37	1.26	Org-N	3	0.15	1.08
	TS	8	0.89	3.03	TS	7	0.80	2.26
	Ash	9	0.89	3.00	Ash	8	0.85	2.56
	PS	8	0.74	1.97	PS	7	0.77	2.07

- 1mm optical path length (PB1) had the greatest  $R^2$  for predicting manure constituents under transmittance mode. Differences between PB2 and PB5 were small.
- $R^2$  and RPD of HS were greater than PB1 for  $\text{NH}_4\text{-N}$  and Org-N, while  $R^2$  and RPD of PB1 were greater than HS for TS, Ash and PS.

Reverse trends of absorbance and water peaks were observed in reflectance and transmittance modes. The transmittance PB2 and PB5 showed only the 1450nm band.

## NMR Results

Table B. Linear fitness of NMR prediction vs. lab measurements for manure nutrients based on overall samples and adjustments of TS groups.

Parameter	RT (min)	$R^2$		
		Overall	TS < 8%	TS > 8%
TS (%)	10 s	0.80	0.86	0.50
	15	0.56	0.94	0.21
TN ( $\text{mg L}^{-1}$ )	30	0.63	0.96	0.18
	45	0.66	0.96	0.21
	60	0.61	0.96	0.23
	90	0.61	0.96	0.23
$\text{NH}_4\text{-N}$ ( $\text{mg L}^{-1}$ )	15	0.94	0.98	0.51
	30	0.96	0.99	0.90
	45	0.97	1.00	0.84
	60	0.97	1.00	0.70
P ( $\text{mg L}^{-1}$ )	30	0.89	0.68	0.91
	45	0.92	0.84	0.87
	60	0.91	0.72	0.90
	90	0.88	0.76	0.84

- Accuracy and precision of the NMR analyzer for predicting TS is affected by solid content range and was more accurate with TS<8%.
- $R^2$  of TN and  $\text{NH}_4\text{-N}$  with TS<8% were significantly greater than TS>8% and  $R^2$  improved as RT increased for TN.
- NMR prediction for TP was not enhanced by increased RT, and effect of TS on TP prediction was not significant.

- RT was not observed to affect precision of NMR predictions for TS, TN,  $\text{NH}_4\text{-N}$ , and TP.
- Intra-sample variations (Rp) of TP were significantly higher than TS, TN, and  $\text{NH}_4\text{-N}$  and higher than its inter-sample variations (Rd) indicating TP prediction of NMR was not precise and robust.

Table C. Analysis of AbsDiff of manure composition at different RTs

Parameter	RT (min)	N	Mean	SD	Rd (%)	Rp (%)
TS (%)	10 s	19	6.1	3.66	60.0	18.6
	15	20	359.9	204.47	56.8	48.6
$\text{NH}_4\text{-N}$ (mg/L)	30	20	337.0	169.02	50.2	42.3
	45	20	312.4	163.62	52.4	33.4
	60	19	306.6	195.16	63.7	31.0
TN (mg/L)	15	19	896.4	407.08	45.4	24.9
	30	19	839.0	373.15	44.5	20.6
	45	19	814.6	327.67	40.2	15.1
TP (mg/L)	60	19	856.0	382.12	44.6	16.3
	30	19	78.3	35.01	44.7	73.9
	45	20	81.6	43.04	52.8	70.2
	60	20	85.2	54.57	64.0	56.6
	90	19	68.4	37.75	55.2	73.4

## Objectives & Method

### NIR

- Can NIRS provide robust prediction models using a spiking method.
- Are changes in NIR spectral data driven by direct variance of N concentration.
- Compare reflectance vs. transmittance.

- Twenty manure samples were assayed for: TS, ash, particle size (PS),  $\text{NH}_4\text{-N}$ , TN, P, and K using standard manure analysis program (MAP) procedures.
- Each sample was spiked with  $\text{NH}_4\text{-N}$  and Org-N, respectively, at 4 levels: 1.25X, 1.5X, 2X, and 4X of N conc. in the control.
- Samples were scanned by a NIR spectrometer with a reflectance sensor (HS) and a transmittance probe (PB).
- Calibrations were developed using partial least-squared (PLS) regression between spectral data and reference values.
- Evaluations were based on coefficient of determination ( $R^2$ ) and residual prediction deviation (RPD).

### NMR

- Assess the accuracy and precision of a low-field NMR manure sensing device for predicting TS,  $\text{NH}_4\text{-N}$ , TN, and P.
- Evaluate the effects of run time (RT) on the accuracy of the measurements.

- Twenty manures samples were assayed for: TS,  $\text{NH}_4\text{-N}$ , TN, P, and K using standard MAP procedures.
- Blended samples with particle size less than 0.5mm were transferred into test tubes and measured by the NMR analyzer.
- TS was analyzed at RT of 10s, TN and  $\text{NH}_4\text{-N}$  were tested at RTs of 15min, 30min, 45min, and 60min, and TP was predicted at RTs of 30min, 45min, 60min, and 90min, respectively.
- Results were assessed based on basic statistics, coefficient of variation (CV), repeatability (Rp), and reproducibility (Rd) of absolute differences ( $| \text{Lab} - \text{NMR} |$ ).

## Conclusions & Future Work

### NIR

- Transmittance probe yielded calibrations that had higher  $R^2$  and RPD for TS, Ash, and PS, and reflectance sensor improved the accuracy  $\text{NH}_4\text{-N}$  and Org-N predictions.
- NIR sensors had potential to predict the N concentrations without being affected by TS, Ash content, and PS of the dairy manure (results not shown).
- Spiking is promising method for a rapid and cost-effective development of prediction models for dairy manure constituents including  $\text{NH}_4\text{-N}$ , Org-N, TS, Ash, and PS using NIR spectroscopy.

### NMR

- NMR predictions of TS,  $\text{NH}_4\text{-N}$ , and TN were accurate for samples TS<8%, but not well correlated to the lab measurements for TS>8%.
- TP predicted by NMR was not affected by TS levels and the overall predictions showed good correlation with lab results. However, TP prediction was not precise and robust.
- Accuracy and precision of NMR were improved by longer RTs for  $\text{NH}_4\text{-N}$ , but not for other parameters.

Further work: Evaluating the NIR system for field application at variable rates; increasing sample space to develop more robust NIR calibrations; recalibrating NMR based on US manure; improving accuracy and precision of NMR for TP.

## Acknowledgement

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