ACS OMEGA

http://pubs.acs.org/journal/acsodf

Article

Fast and Accurate Quantification of Nitrogen and Phosphorus Constituents in Animal Slurries Using NMR Sensor Technology

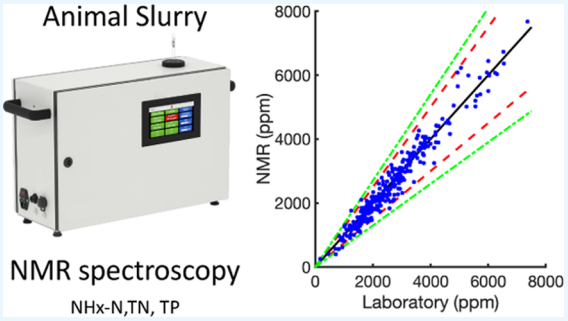
Ole N. Jensen, Michael Beyer, Morten K. Sørensen, Maria Kreimeyer, and Niels Chr. Nielsen*

Cite This: *ACS Omega* 2021, 6, 17335−17341

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: The optimal processing of animal slurry with a minimal environmental impact either as an organic fertilizer or as an energy source for biogas production fundamentally requires accurate, fast, cost-effective, and mobile analytical techniques for the measurement of nitrogen and phosphorus in large volumes of liquid animal slurry. Based on more than 300 different slurries from different species and origins, we provide here an extensive analysis of low-field NMR and standard laboratory measurements for animal slurry analysis. It is found that low-field NMR provides higher precision than wet chemistry laboratory measurements for ammonium nitrogen and total nitrogen, while it provides slightly lower precision for total phosphorus measurements. Low-field NMR may, through a square-root dependency between time and precision, be adapted for analysis at farms, in slurry tankers/transporters, in biogas digesters, or in laboratories.



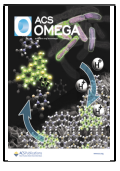
1. INTRODUCTION

Cost-efficient, accurate, fast, mobile, and operationally simple sensors to provide detailed information on nitrogen and phosphorus constituents in animal slurry are in urgent need. Such sensors will enable the optimization of yields of crops in farming, sustainable animal production, and the production of biogas and organic fertilizers from agricultural-based biogas facilities. They will also ensure a minimal environmental footprint and adherence to increasingly tight regulations related to the agricultural use of animal slurry as an organic fertilizer. To acquire the needed information, sensors should be available for operation in all relevant parts of the animal slurry value chain spanning from slurry tanks at the farmers site, via slurry spreaders/transporters and biogas/biorefinery/wastewater plants, to analytical laboratories. Most measurements are currently made at the laboratories. Furthermore, for regulation purposes, it may be desirable to combine measurements with direct reporting to authorities at the desired measuring points and to supplement with sensors mapping the state of the environment.

The current extensive use of specialized laboratories to analyze a huge series of slurry samples from farms, for example, in relation to the transport of manure between regions, is costly, time-consuming, and fails to provide real-time data desirable for precision farming. Traditional laboratory methods for animal slurry analysis[1,2] include wet-chemistry-based titration methods for the determination of ammonium (NHx-N), Kjeldahl or combustion methods for the determination of total nitrogen (TN), and ICP for the determination of total phosphorus (TP) which all are practically demanding or time consuming. Accordingly, it is important to carefully investigate the applicability of different measurement methods including those proposed to supplement laboratory methods with easier alternatives and real-time analytical methods. This will minimize the need for the transport of slurry samples from farms to laboratories and will enable an increase in the volume of measurements needed for nutrient administration and regulation. In the evaluation of potential methods, it is also important to address changes related to sample heterogeneity (e.g., slurry, solid manure, straws, and so forth) impacting measurements through different locations of ions (e.g., NHx-N and free phosphates) and dry matter constituents (organic phosphate and nitrogen) and therefore also sample preparation.[1,2]

Substantial efforts have been devoted recently to launching near-infrared spectroscopy (NIRS) for manure,[3−5] animal slurry,[6,7] and organic fertilizer[8] analyses to enable fast, on-site measurement. This is despite challenges in providing sufficient precision, determination of phosphorus, and analyzing the prevailing liquid-type animal slurry. Furthermore NIRS—as an indirect method—is highly dependent on accurate and regularly updated databases with animal slurries of similar type and origin, which may be difficult to obtain and maintain for general farming applications. To overcome such challenges,

Received: March 17, 2021
Accepted: June 17, 2021
Published: June 29, 2021



we recently proposed low-field nuclear magnetic resonance (NMR) spectroscopy as a versatile direct method for N, P, and K analyses of organic fertilizers.[9] This first study was based on the data for a small set of representative samples of animal slurries from different species and origins. In this paper, we extend this study to include a much larger body of statistical materials of samples, present a new approach to determine TN, and provide a detailed comparison with laboratory measurements. Based on the samples and associated data from laboratory measurements, we assessed the precision of low-field NMR and traditional laboratory measurements and describe the flexibility of low-field NMR to operate at laboratories as well as on mobile devices depending on the desired precision for the chosen application.

2. MATERIALS AND METHODS

2.1. Samples. The present study is based on more than 300 different slurry samples from different species obtained from AGROLAB (Sarstedt, Germany) anonymized, and with known data on NHx-N, TN, TP, total solids/dry matter (TS), and pH. Table 1 provides an overview of the animal slurry samples analyzed in terms of types (species), numbers, and average compositional values, as provided from standard laboratory analysis (see Supporting Information, Table S1 for a detailed list of laboratory and NMR results for all the samples). The samples were taken from animal slurries, then laboratory analyzed (Agrolab, Sarsted, Germany), and thereafter sent frozen in an anonymized form to NanoNord (Aalborg, Denmark) for NMR analysis. The samples originate from different specified animal species, as well as samples of unknown type (e.g., from farms not separating slurries according to species) and slurries from biogas digesters. The samples are primarily of German origin but also include samples from the surrounding countries. In the present study, neither the species nor the geographical origin of the samples was taken into account for neither the laboratory nor the NMR analysis to demonstrate the broad applicability of both methods without a need for calibrations or database corrections.

Table 1. Manure Samples Analyzed

type	# samples	⟨NHx-N⟩ (ppm)[a]	⟨TN⟩ (ppm)[a]	⟨TP⟩ (ppm)[a]	⟨TS⟩ (%)[a]
pig	97	3047	4406	1073	5
cattle	104	1842	3419	577	7,3
digester	68	3286	5132	802	6,4
unknown	49	2641	4113	807	5,4
total	318	2805	4330	687	5,5
mixtures[b]	79	2647	4230	850	6,3

[a]Average values of ammonium (NHx-N), TN, TP, and total solids (TSs). [b]Mixtures using six original laboratory samples in equal quantity w/w without any sample being present in more than one mixture; mixed samples were used to unravel statistical variations in laboratory measurements.

2.2. Protocol for Analysis. Figure 1 outlines the protocol and definitions used in analysis of 318 different slurries and 79 mixtures, as listed in Table 1 (cf. Table S1). The 79 physical mixtures were generated each using six original samples (each with equal quantity; no samples were included more than in one mixture) sorted according to the laboratory TP value to span as much as possible the full range of TP (and associated with this to a large extend TN) values. We focus here exclusively on NHx-N, TN, and TP measurements, keeping in mind that information about free phosphates (PO_4−P), TS, pH, and potassium (K) may be established for the same samples using the presented NMR technology.

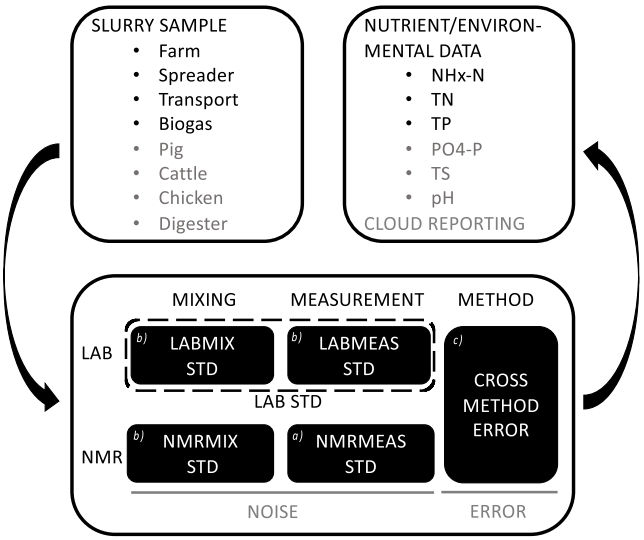


Figure 1. Protocol used in the analysis of animal slurries and mixtures as described in Tables 1 and S1. Definition of samples, parameters, and assessment of noise (standard deviation, STD) and error contributions to laboratory (LAB) and NMR measurements (NMR) providing nutrition/environmental information on animal slurries as an organic fertilizer and source for biogas production. See text for further description.

2.3. Laboratory Analysis. For each of the 318 manures, laboratory analysis involved titration, Kjeldahl or dry combustion methods, and ICP for the determination of NHx-N, TN, and TP, respectively, supplemented with drying (105 °C for 16 h) to determine dry matter and pH measurement.

2.4. NMR Analysis. For all the samples, NMR signals were acquired using ^{14}N QCPMG[10] and ^{31}P CPMG[11] experiments supplemented with ^{1}H CPMG and inversion-recovery CPMG experiments on 1.4 (25 mm bore) and 1.5 T (20 mm bore) TVESKAEG low-field NMR sensors in a robotic system with 20 instruments operated in parallel on all the samples to document experimental robustness (see setup in Figure S1). For each CPMG experiment, ^{14}N and ^{31}P signal intensities and ^{1}H T_1 and T_2 relaxation data were obtained through the fitting of the decaying time-domain echo signal envelope to single- or double exponential decay functions and with the overall intensity reference to a calibrated standard (see details in the Supporting Information). Figure 2 shows examples of decays for (a) ^{14}N QCPMG, (b) ^{31}P CPMG, and (c) ^{1}H CPMG for an animal slurry sample with circles (blue) representing experimental echo intensities and lines (red) representing numerically fitted exponential decays (details in the Supporting Information).

The sample preparation for the NMR measurements is extremely simple, which is an important asset when considering the method for large-scale analysis. It amounts to first blending the slurry in the 1/2−1 L containers received from the laboratory analysis, next sucking the samples up in the 8 mm i.d. sample tubes to a sample length of 42 mm (around 2.1 mL of the sample; the sample tube operates as a syringe

https://doi.org/10.1021/acsomega.1c01441
ACS Omega 2021, 6, 17335−17341

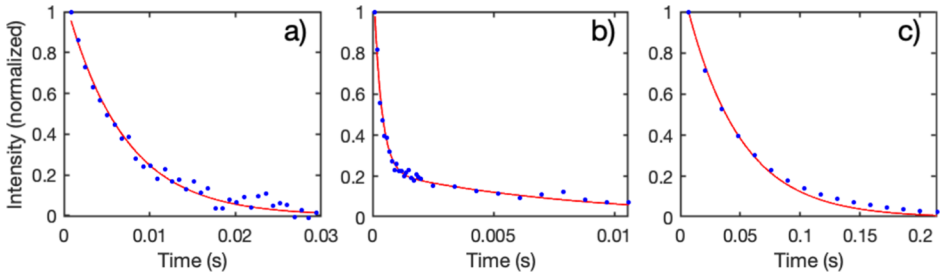


Figure 2. Representative (a) 30 min ^{14}N QCPMG, (b) 60 min ^{31}P CPMG, and (c) 10 s ^{1}H CPMG experimental data (filled circle, blue) and fitted curves (line, red) for an animal slurry sample. The fitted curves (normalized to the intensity of the first point of the experiment) represent the intensity and relaxation parameters of (a) I = 1.08, T_2 = 6.79 ms, (b) I_1 = 1.03, T_{21} = 315 μs, I_2 = 0.23, T_{22} = 8.1 ms, and (c) I = 1.12, T_2 = 48.5 ms (see definitions in the Supporting Information).

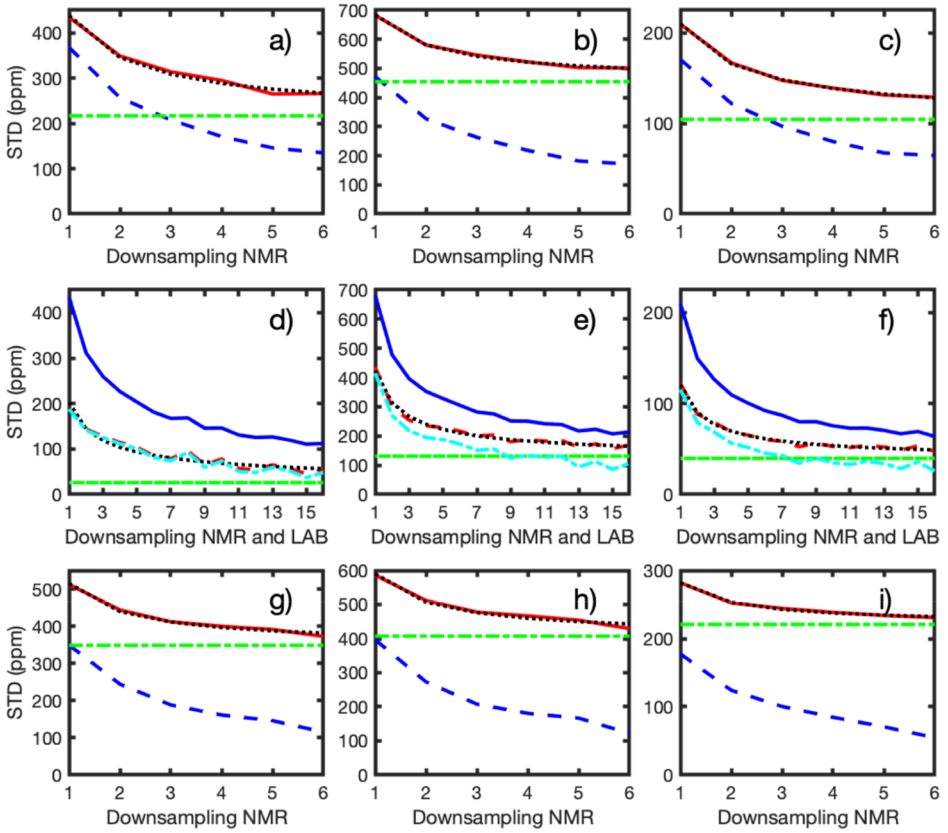


Figure 3. Noise STD and error analysis for ammonium (NHx-N) (left; a,d,g), TN (middle; b,e,h), and TP (right; c,f,i) measurements using low-field NMR and laboratory analyses for 318 animal slurries (a−f) and 188 duplicates (g−i). All graphs show the observed STD/error along the vertical axis and downsampling (n) along the horizontal axis, which for (a−c and g−i) is expressed as a factor to unit NMR measurement times of 5 min for nitrogen (left, middle) and 10 min for phosphorus (right) and for (d−f) describes simultaneously downsampling for laboratory and NMR measurements with the factor expressing the number of samples over which both NMR and laboratory data are averaged. (a−c) Experimental (solid line, red) and fitted (dotted line, black) total STD along with the resulting curves for s_{NMRMEAS} (dashed line, blue) as well as $s_{\text{LAB-NMRMIX}}$ and $s_{\text{CROSSMETHOD}}$ (dot-dashed line, green). (d−f) Downsampled (solid line, blue) total STD which after the subtraction of effects from s_{NMRMEAS} leads to $s_{\text{LAB-NMRMIX}}$ and $s_{\text{CROSSMETHOD}}$ (dashed line, red). The latter curve is fitted (dotted line, black) to give curves for $s_{\text{LAB-NMRMIX}}$ (dot-dashed line, cyan) and $s_{\text{CROSSMETHOD}}$ (long-dashed line, green). (g−i) Total STD for downsampled NMR experiments obtained for two sets of samples (duplicates) of the same slurries (solid line, red), which is fitted (dotted line, black) to provide s_{NMRMEAS} (dashed line, blue) and s_{NMRMIX} (dot-dashed line, green).

facilitating the process), and finally inserting the tube into a spectrometer individually by hand, using a sample changer, or by the robot in the robotic setup as used in this study. On each spectrometer, each sample is analyzed using 5 min ^{14}N QCPMG (for NHx-N and TN), 3.3 min ^{1}H CPMG and inversion-recovery CPMG (for TN), and 10 min ^{31}P CPMG (for TP) experiments. The collection of NMR data from all instruments in the robotic system allows total measurement times from 5 to 100 min for ^{14}N and 10 to 200 min for ^{31}P for each sample, enabling detailed analysis of measuring precision as a function of time. Further details on the experiments are given in the Supporting Information.

3. RESULTS AND DISCUSSION

Based on the large set of animal slurries, we have demonstrated the general applicability of low-field NMR for slurry analysis

https://doi.org/10.1021/acsomega.1c01441
ACS Omega 2021, 6, 17335−17341

and have in detail accessed the precision of NMR in comparison with laboratory analysis—both of which, besides the intrinsic uncertainty of the applied measuring technique, are influenced by uncertainties arising from picking out/handling/mixing representative samples.

Following the notation shown in Figure 1, the STD (noise and error) of an NMR measurement relative to the corresponding laboratory measurement may be expressed as

$$s = \sqrt{{s_{\mathrm{NMR}}}^2 + {s_{\mathrm{LAB}}}^2 + {s_{\mathrm{CROSSMETHOD}}}^2} \quad (1)$$

where the NMR STD (s_{NMR}) and laboratory STD (s_{LAB}) both contain contributions from sample preparation (MIX) and measurement/instrument (MEAS)

$$s_{\mathrm{NMR}} = \sqrt{{s_{\mathrm{NMRMIX}}}^2 + {s_{\mathrm{NMRMEAS}}}^2} \quad (2a)$$

$$s_{\mathrm{LAB}} = \sqrt{{s_{\mathrm{LABMIX}}}^2 + {s_{\mathrm{LABMEAS}}}^2} \quad (2b)$$

The cross method error ($s_{\mathrm{CROSSMETHOD}}$) describes systematic errors between the two measurement methods which cannot be accounted for as a statistical noise STD of the two methods individually. The STD is defined as $s = \sqrt{\frac{1}{m-1}\sum_{i=1}^{m}(x_i - \bar{x})^2}$, where x_i is the variable (e.g., difference between NMR and laboratory measurement) and $\bar{x}$ the mean value over m data points (i.e., number of measurements). In the following, on the basis of experimental NMR and laboratory measurements, we will derive values for various components for the determination of NHx-N, TN, and TP contents in animal slurries.

The NMR measurement STD (s_{NMRMEAS}, marked a in Figure 1) may readily be determined using NMR data spanning the range of 5−30 min for ^{14}N and 10−60 min for ^{31}P and, knowing the relationship that doubling the NMR time will reduce the STD induced by the white noise by $\sqrt{2}$. This concept may be extended such that increasing the measurement time by a factor of n will reduce the STD of the part of the signal that is governed by the statistical (white) noise by $\sqrt{n}$. The constant part that will not follow this dependency will be attributed to STD or ERROR from other sources than those influenced by the downsampling variable n. This can be expressed in terms of the functionality

$$s(n) = \frac{r}{\sqrt{n}} + q \quad (3)$$

We call this downsampling by a factor of n, as this concept also applies to the laboratory measurements as we shall see in the following.

Determination of s_{NMRMEAS} is demonstrated in Figure 3a−c, where the solid line red curves represent the total STD (s) observed for the difference between NMR and laboratory measurements for all nonmixed samples (normalized to slope 1 in a NMR vs laboratory data correlation) for NHx-N, TN, and TP as a function of time (downsampling data through time extended by the factors given in the horizontal axis). This curve may be fitted (dotted black line) to obtain values for s_{NMRMEAS} (marked a in Figure 1) and the combined LAB-NMRMIX STD ($s_{\mathrm{LAB\text{-}NMRMIX}} = \sqrt{{s_{\mathrm{LAB}}}^2 + {s_{\mathrm{NMRMIX}}}^2}$, marked b in Figure 1) and $s_{\mathrm{CROSSMETHOD}}$ (marked c in Figure 1). The two components (r and q in eq 3) are represented by blue dashed and green dot dashed lines in Figure 3a−c, respectively. This leads to s_{NMRMEAS} values of 110, 147, and 74 ppm per hour for NHx-N, TN, and TP, respectively, while the corresponding combined $s_{\mathrm{LAB\text{-}NMRMIX}}$ and $s_{\mathrm{CROSSMETHOD}}$ values (marked b and c in Figure 1) are added to 217, 455, and 104 ppm, respectively.

To determine the $s_{\mathrm{LAB\text{-}NMRMIX}}$ and $s_{\mathrm{CROSSMETHOD}}$ STDs, we exploit the fact that laboratory measurements may also be characterized by variations (STD), which may be discriminated as a statistical (white noise) STD and a nonstatistical STD/error term (r and q in eq 3, respectively). Following this argument, we added in digital mixing of laboratory measurements, as illustrated in Figure 3d−f. In this case, downsampling by a factor of n (number on horizontal axis) corresponds to digital averaging data from both laboratory and NMR measurements over the same m samples with one sample only represented once in the data set and averaging performed such a uniform distribution is obtained from low to high TP and TN values.

Through digital mixing of laboratory data, we obtain information about the noise from the mixing (sample preparation) and measurement for the laboratory analysis as well as cross method error for both laboratory and NMR analysis. In this case, the solid blue line represents the total STD, while the dashed red line represents the total STD without the contribution from s_{NMRMEAS} (i.e., combined $s_{\mathrm{LAB\text{-}NMRMIX}}$ and $s_{\mathrm{CROSSMETHOD}}$). Among these, the former is reduced by $\sqrt{n}$ upon downsampling, while the latter is constant. From fitting (dotted black line), we obtain $s_{\mathrm{LAB\text{-}NMRMIX}}$ (collectively marked b in Figure 1) values of 241, 464, and 114 ppm and corresponding $s_{\mathrm{CROSSMETHOD}}$ values of 26, 131, and 40 ppm.

Information about the noise induced by the mixing process in the NMR measurements (s_{NMRMIX}), and through this getting a clean measure for the laboratory noise s_{LAB} (both measurement and mixing), may be obtained by measuring duplicates of the samples (two samples taken out for a representative set of animal slurry samples obtained from Agrolab and mixtures made at NanoNord) by NMR. This is illustrated in Figure 3g−i, where the solid red line represents the total STD taken for the difference between the measurements obtained for the two sets of samples A and B. Through fitting (dotted black line), we obtain s_{NMRMEAS} (dashed blue line), in this case representing one set of the duplicates, and the combined contributions from s_{NMRMIX} and the noise associated with the nondownsampled NMR measurement being the other set of duplicates (dot dashed green line). The former values match well with those obtained in Figure 3a−c, while s_{NMRMIX} amounts to 85, 85, and 99 ppm for NHx-N, TN, and TP, respectively. This leads to the combined measurement and mixing STDs (s_{LAB}) for the laboratory measurements of 225, 456, and 56 ppm for NHx-N, TN, and TP, respectively. We note that the present data do not allow subdivision into s_{LABMIX} and s_{LABMEAS}.

Table 2 lists the STD/error values extracted from Figure 3. We note that the values are based on accumulated 5 min ^{14}N and 10 min ^{31}P measurements and may, for the NMR part, improve with longer measuring times with enhanced signal noise, in particular, at low concentrations. In relation, we point out that the NMR measurement STD (s_{NMRMEAS}) represents a balance between time and precision and can be adapted to a given application using the relationship that increasing/decreasing time by a factor of 4 decreases/increases the STD by a factor of 2. Finally, we note that according to eqs 1, 2a, and 2b the numbers are not additive but are related through a square root of the sum of squared numbers.

https://doi.org/10.1021/acsomega.1c01441
ACS Omega 2021, 6, 17335−17341

Table 2. Noise and Error STDs Associated with Low-Field NMR and Laboratory Measurements of Animal Slurry Samples[a]

parameter	$s_{NMRMEAS}$[b] (ppm)	s_{NMRMIX} (ppm)	s_{NMR}[b] (ppm)	s_{LAB} (ppm)	$s_{CROSSMETHOD}$ (ppm)
NHx-N	110	85	139	225	26
TN	147	85	170	456	131
TP	74	99	124	56	40

[a]See definitions of STDs in Figure 1 and text. [b]STD corresponding to 1 h measurement time.

As revealed by the numbers listed in Table 2, which for the NMR part is represented by STD values for 1 h measurements, low-field NMR provides higher precision for NHx-N and, in particular, TN than the present laboratory measurements, while it is associated with a slightly lower precision for TP. It should, however, be noted that the NMR measurements are substantially easier to perform than typical laboratory measurements. In relation to TP, it is evident that a dominant fraction of the NMR STD comes from mixing, most likely due to the unequal presence of particles in samples or due to effects from precipitation.[1,2] This implies that the precision may readily be improved statistically by measuring strategies based on several sample tubes or measurements in a flow setup as, for example, relevant on transport vehicles. Low-field NMR instrumentation for flow measurements is available and, with regards to precision, is on par with the benchtop instruments.

A more direct view of the comparison between NMR and laboratory parameters and the repeatability of NMR experiments may be obtained from Figure 4, and the associated parameters are summarized in Table 3 (marked 1:1 to reflect the comparison of single samples). The upper panels in Figure 4 show laboratory data along the horizontal axis and NMR data along the vertical axis, while the lower panels show data from the duplicate NMR experiments with the data for the two subsequent measurements on the same sample (i.e., repeats of measurements) with the vertical axis representing the first measurement correlated to the average of the two measurements along the horizontal axis. In this case, the NMR measurement time is 40 min for ^{14}N (left and middle columns) and 80 min for ^{31}P experiments (right column). It is evident that NMR data correlate well with the laboratory as expressed though R^2 values in the range of 0.97−1.00 and deviations in the range 9.8−18.9% (see Table 3 for details), where we recall that both NMR and laboratory measurements contribute to the deviation. The red dashed and dot dashed lines represent ±25 and ±35% deviations. The NMR versus NMR average duplicate correlations shown in the bottom row leads to NMR STD duplicate values, $s_{dupl} = \sqrt{\frac{1}{2m}\sum_{i=1}^{m}(x_i^A - x_i^B)^2}$ in the order of 37−106 ppm. Values for s_{dupl}, the repeatability $s_r = 2\sqrt{2}s_{dupl}$, and the normalized repeatability $s_r/(\overline{x^A - x^B})\cdot 100\%$ are also included in Table 3. The red dashed lines represent accreditation limits proposed in the Dutch Implementation Regulation for Fertilization Act[12] (see caption for details).

The effect of partially averaging the laboratory STD through physical mixing of samples becomes clearly apparent by comparing Figure 4 with the corresponding Figure 5 showing the same type of correlations; however, in this case for NMR data recorded on samples obtained by mixing six samples, averaging the laboratory data, and recording NMR data on the mixed sample. It is seen from the upper panels in Figure 5 (and the corresponding numbers listed in Table 3, marked 6:1), that the NMR versus laboratory correlations improve substantially with deviations reducing to 7.4, 5.9, and 11.7% for NHx-N, TN, and TP, respectively, as summarized in Table 3. As expected, the corresponding NMR versus NMR duplicate analysis results in parameters quite similar to those observed for the native nonmixed samples, ending up at 2.5, 2.4, and

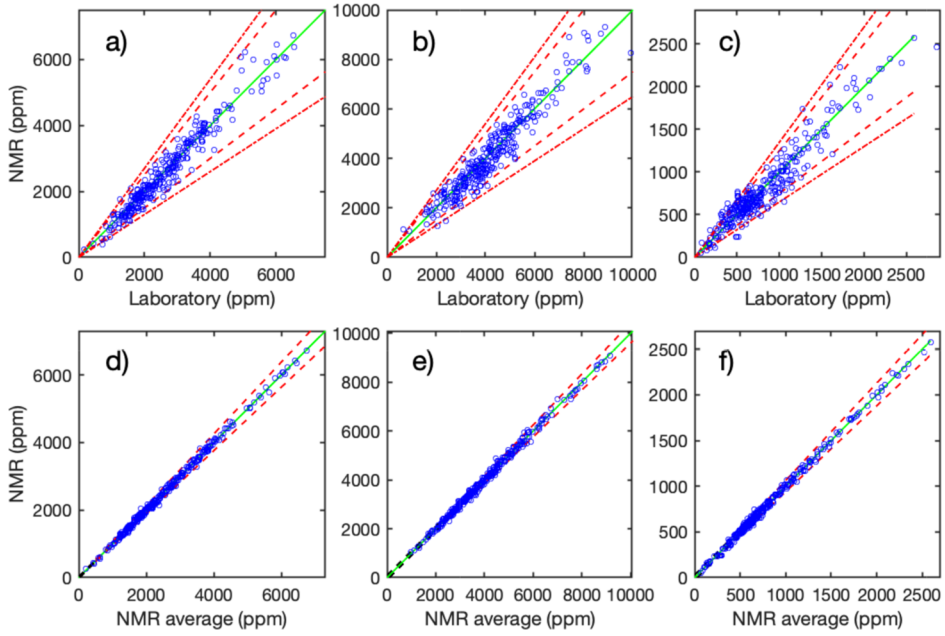


Figure 4. Correlations between NMR and laboratory data (a−c; red dashed and dot dashed lines represent ±25 and ±35%, respectively) and duplicate NMR analysis (NMR data for two sets of samples correlated) (d−f; red dashed lines[12] represents ±100 ppm up to 2500 ppm and ±4% above 2500 ppm for d,e and ±30 ppm up to 500 ppm and ±6% above 500 ppm for f) for ammonium (NHx-N) (a,d), TN (b,e), and TP (c,f). The NMR data represent 2 h of measurement time for each sample (40 min ^{14}N and 80 min for ^{31}P).

https://doi.org/10.1021/acsomega.1c01441
ACS Omega 2021, 6, 17335−17341

Table 3. Correlation of NMR and Laboratory Measurements for Animal Slurries[a]

					NMR vs laboratory			NMR duplicate (NMR vs NMR)				
parameter	# samples[b]	min[b] (ppm)	max[b] (ppm)	average[b] (ppm)	R^2	STD (ppm)	% dev (%)[c]	R^2	s_{dupl} (ppm)	% dev (%)[c]	s_r (ppm)	s_r normalized (%)[d]
NHx-N 1:1	318	175	7362	2643	0,97	216	9,8	0,97	85	2,8	242	9,1
NHx-N 6:1	79	1180	5739	2647	0,98	169	7,4	0,98	77	2,5	217	8,2
TN 1:1	318	654	9906	4195	0,92	415	11,8	1	106	2,5	300	7,2
TN 6:1	79	1833	8094	4231	0,96	221	5,9	1	97	2,4	274	6,5
TP 1:1	318	75	2856	810	0,93	113	18,9	1	37	4,5	104	12,9
TP 6:1	79	228	2398	850	0,94	91	11,7	1	35	3,7	99	11,6

[a]The results relate to Figures 4 and 5 representing 1:1 laboratory and NMR measurements and 6:1 laboratory and NMR measurements (six laboratory samples were mixed, laboratory data averaged, and NMR analysis performed on the mixed sample), respectively. The parameters correspond to 40 min ^{14}N and 80 min ^{31}P measurement times. [b]Numbers correspond to NMR versus laboratory/NMR duplicate analysis. [c]The deviation is defined as the STD (see the formula below eq 2b) with $x_i = (lab_i - nmr_i) \times 100/lab_i$. [d]Calculated as $s_r \times 100$/average.

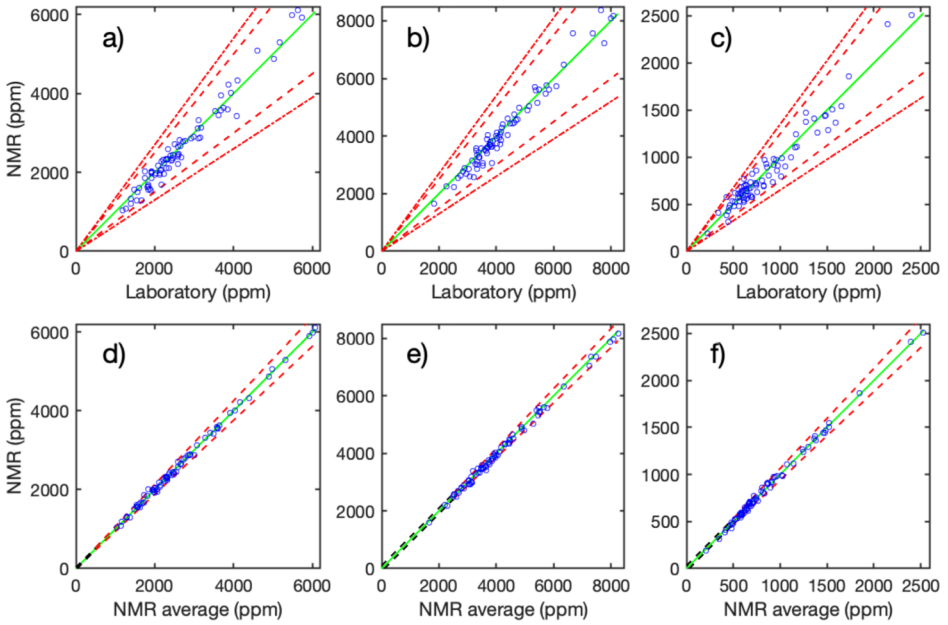


Figure 5. Correlations between NMR and laboratory data (a–c) and duplicate NMR analysis (d–f) performed on 79 samples obtained by mixing 6 original samples, averaging the laboratory data, and performing NMR analysis. Arrangement as shown in Figure 4.

3.7% for NHx-N, TN, and TP, respectively. As supported by the dashed lines in the repeatability plots in Figures 4 and 5, we note that the last two numbers compare favorably with the laboratory accreditation limits issued in the Dutch Fertilizer Act (focusing only on TN and TP)[12] being 4 and 6% for TN and TP in the range of over 2500 and 500 ppm, respectively.

While the primary objective of this study is not the evaluation of laboratories, it is relevant to discuss our results relative to a recent study, evaluating results from eight American certified manure analysis laboratories as well as supplementary results obtained from another European laboratory. Taking the first view, Sanford et al.[13] recently reported TN, NHx-N, and TP values obtained for four different animal slurry samples measured at eight randomly selected certified American manure analysis laboratories [related to the Manure Analysis Proficiency (MAP) program].[14] For quite similar content of NHx-N (965–1650 ppm, mean 1218 ppm), the STD of the laboratory measurements is 211 ppm, which may be compared with an NMR STD (including mixing) of 139 ppm for 1 h (based on 5 min measurements). For TN (2338–4223 ppm, mean 2878 ppm), the STD of the laboratory measurements is 371 ppm to be compared with 170 ppm for 1 h (based on accumulated 5 min measurements). For TP, the samples in the laboratory comparison differ more (378–4040 ppm, mean 1308 ppm) leading to an average laboratory STD of 239 ppm to be compared with an NMR STD of 124 ppm for 1 h (based on accumulated 10 min measurements). We note that the NHx-N and TN STDs in the study of Sanford et al.[13] are very similar to those we found in our analysis (Table 1), noting that we examine a much larger set of samples with a much larger span of concentrations. For TP, the STD in the American analysis is substantially larger than what we observe, with variations being particularly pronounced for a sample with high TP content.

To assess further repeatability for TN and TP measurement, 50 samples in duplicate were analyzed by Dumea (Wijhe, The Netherlands). For these samples, the repeatability (s_r) and normalized repeatability (s_r/average × 100%) for TN were determined to 392 ppm and 9.4% (average TN for samples 4187 ppm). In comparison, the NMR repeatability (Table 2) is favorably characterized by the values 274 ppm and 6.5% for TN. For TP, the analysis at Dumea leads to repeatability and

https://doi.org/10.1021/acsomega.1c01441
ACS Omega 2021, 6, 17335–17341

relative repeatability values of 120 ppm and 13.8% (average TP for samples 872 ppm), to be compared with the more favorable NMR repeatability of 99 ppm and 11.6%.

4. CONCLUSIONS

In conclusion, we have presented a detailed evaluation of low-field NMR analysis relative to laboratory measurements for a large set of animal slurry samples. Using this setup, we were able to delineate the precision of low-field NMR analysis of manure samples, as the major objective, and obtain information at the level of precision in a typical laboratory analysis setup as the secondary objective. Our analysis reveals that low-field NMR overall provides the same level of accuracy as the laboratory measurements. A great advantage of the NMR technology is that it is flexible for laboratory as well as mobile applications on farm sites, animal slurry/manure transporters, and slurry spreaders. Furthermore, in all cases, the low-field NMR method is much faster and easier in terms of sample handling than typical laboratory analysis involving wet chemistry methods. It can readily be adapted for on-line field analysis with a proper balance between precision and measuring times for different parameters. We have in this study focused on NHx-N, TN, and TP measurements but should note that information about parameters such as pH, dry matter (TS), and potassium may also be provided using low-field NMR spectroscopy.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c01441.

Details on samples, laboratory analysis, sample preparation, NMR experiments, and numerical fitting, a robot system with 30 low-field NMR sensors, schematic illustration of sampling and fitting of CPMG data for two sample constituents, and laboratory and NMR results for 379 animal slurry samples (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Niels Chr. Nielsen − *NanoNord A/S, DK-9220 Aalborg Ø, Denmark;* Present Address: Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, DK-8000 Aarhus C, Denmark.; orcid.org/0000-0003-2978-4366; Email: ncn@nanonord.dk

Authors

Ole N. Jensen − *NanoNord A/S, DK-9220 Aalborg Ø, Denmark*

Michael Beyer − *NanoNord A/S, DK-9220 Aalborg Ø, Denmark*

Morten K. Sørensen − *NanoNord A/S, DK-9220 Aalborg Ø, Denmark; Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark; Department of Biological and Chemical Engineering, Aarhus University, DK-8200 Aarhus N, Denmark;* orcid.org/0000-0001-8263-555X

Maria Kreimeyer − *AGROLAB Agrar und Umwelt GmbH, DE-31157 Sarstedt, Germany*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c01441

Author Contributions

The manuscript was written through contributions of all the authors.

Notes

The authors declare the following competing financial interest(s): Filled a patent in the area. The authors O.J., M.B., M.K.S., and N.C.N. are affiliated with NanoNord A/S selling the TVESKAEG NMR sensor for industrial and scientific applications.

■ ACKNOWLEDGMENTS

We thank Dr. R. Sanford, University of Wisconsin, for addressing our attention to the American Manure Analysis Proficiency program and ref 13.

■ REFERENCES

(1) Sommer, S. G.; Christensen, M. L.; Schmidt, T.; Jensen, L. S. *Animal Manure Recycling: Treatment and Management*; John Wiley & Sons Ltd.: Chichester, West Sussex, 2013.

(2) Peters, J.; Combs, S. M.; Hoskins, B.; Jarman, J.; Kovar, J. L.; Watso, M. E.; Wolf, A. M.; Wolf, N. *Recommended Methods of Manure Analysis*; Cooperative Extension Publishing: Madison, Wisconsin, USA, 2003.

(3) Reeves, J. B., III; Van Kessel, J. S. Near-infrared spectroscopic determination of carbon, total nitrogen, and ammonium-N in dairy manures. *J. Dairy Sci.* **2000**, *83*, 1829−1836.

(4) Chen, L.; Xing, L.; Han, L. Review of the application of near-infrared spectroscopy technology to determine the chemical composition of animal manure. *J. Environ. Qual.* **2013**, *42*, 1015−1028.

(5) Jancewicz, L. J.; Swift, M. L.; Beauchemin, K. A.; Koenig, K. M.; Chibisa, G. E.; He, M. L.; McKinnon, J. J.; Yang, W.-Z.; McAllister, T. A. Development of near-infrared spectroscopy calibrations to estimate fecal composition and nutrient digestibility in beef cattle. *Can. J. Anim. Sci.* **2017**, *97*, 51−64.

(6) Sørensen, L. K.; Sørensen, P.; Birkmose, T. S. Applications of feflectance near infrared spectroscopy for animal slurry analysis. *Soil Sci. Soc. Am. J.* **2007**, *71*, 1398−1405.

(7) Cabassi, G.; Cavalli, D.; Fuccella, R.; Marino Gallina, P. Evaluation of four NIR spectrometers in the analysis of cattle slurry. *Biosyst. Eng.* **2015**, *133*, 1−13.

(8) Wang, C.; Huang, C.; Qian, J.; Xiao, J.; Li, H.; Wen, Y.; He, X.; Ran, W.; Shen, Q.; Yu, G. Rapid and accurate evaluation of the quality of commercial organic fertilizers using near infrared spectroscopy. *PLoS One* **2014**, *9*, No. e88279.

(9) Sørensen, M. K.; Jensen, O.; Bakharev, O. N.; Nyord, T.; Nielsen, N. C. NPK NMR sensor: Online monitoring of nitrogen, phosphorous, and potassium in animal slurry. *Anal. Chem.* **2015**, *87*, 6446−6450.

(10) Larsen, F. H.; Jakobsen, H. J.; Ellis, P. D.; Nielsen, N. C. Sensitivity-enhanced quadrupolar-echo NMR of half-integer quadrupolar nuclei. Magnitudes and relative orientation of chemical shielding and quadrupolar coupling tensors. *J. Phys. Chem. A* **1997**, *101*, 8597−8606.

(11) Meiboom, S.; Gill, D. Modified spin-echo method for measuring nuclear relaxation times. *Rev. Sci. Instrum.* **1958**, *29*, 688−691.

(12) Implementation Regulation for the Fertilizers Act (UMW, 2015) Appendix H (APO5). https://wetten.overheid.nl/BWBR0018989/2020-10-08#BijlageH.

(13) Sanford, J. R.; Larson, R. A.; Digman, M. F. Assessing certified manure analysis laboratory accuracy and variability. *Appl. Eng. Agric.* **2020**, *36*, 905−912.

(14) Floren, J.; Miller, R. O.; Montgomery, B. *Manure Analysis Proficiency (MAP) Program Final Report*, 2006. Appendix A https://www.mda.state.mn.us/sites/default/files/inline-files/mapreport01-07ADA.pdf.