Supporting Information for

NPK NMR Sensor: Online Monitoring of Nitrogen, Phosphorus, and Potassium in Animal Slurry

Morten K. Sørensen,[†,] Ole Jensen,[‡] Oleg N. Bakharev,[†] Tavs Nyord,[§] and Niels Chr. Nielsen[†]*

[†]Center for Insoluble Protein Structures (inSPIN), Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Gustav Wieds Vej 14, Aarhus C, DK-8000, Denmark, [‡]NanoNord A/S, Skjernvej 4A, Aalborg Ø, DK-9220, Denmark, [§] Department of Engineering, Aarhus University, Hangøvej 2, Aarhus N, DK-8200, Denmark

* Corresponding author (moks@inano.au.dk)

Table of Content:

Samples and laboratory analysis

As described in the Main text, samples of 16 animal slurries (approximately 20 liter of each) were collected from different farms and biogas plants. See Table S1 for an overview of the samples. From local farms were collected five different cattle slurries, five pig slurries, and three mink slurries, while three digestates from biogas plants using anaerobically co-digested slurries to produce methane, were also included. Of the three digestates, one was originating mainly from pig slurry, one mainly from cattle slurry, and one from mixed slurry as indicated in Table S1. Duplicate samples were made for all 16 slurries to give 32 slurry samples. Furthermore, eight samples of NPK solutions were included. Samples 17, 18, 37, and 39 (see Table S1) were prepared from NH_4Cl, K_2HPO_4, KH_2PO_4, and KCl dissolved in water, whereas samples 38, 40, 19, and 20 were prepared as dissolutions of samples 17, 18, 39, and 37, respectively. Hereby a total of 40 samples were included.

For laboratory analysis, aliquots of each sample were packed in 500 or 1000 ml containers to send for external laboratory analysis. In order to ensure homogeneous subdivisions, the samples were distributed into subsamples (aliquots) by the following procedure: First the 20-liter sample was agitated, and during continued stirring several cups of slurry were taken and divided in three buckets. The slurry was blended in each bucket to fragmentize larger substances like straw and similar in the slurry. During stirring, slurry was taken from the buckets and divided in minor portions to the sample containers for external (laboratory) and internal (NMR) examinations.

The subsamples in 500 or 1000 ml containers (about 3/4 full) were packed with cool packs in insulated boxes, and sent for external analysis at five different laboratories (two Danish, two German, and one Dutch laboratory). Samples 1-20 were sent shortly after packaging, while the duplicate

samples numbered 21-40 were sent to the same laboratories approximately three weeks later to validate that no significant changes of the analyzed parameters were observed due to the time delay of the measurements. All samples were at all laboratories analyzed for dry matter, ammonium N, total N, total P, and K contents. At four laboratories for sample 1-20 and three laboratories for samples 21-40, pH was also measured. Table S1 summarizes the obtained results for all samples. Some of the laboratory results were reported in gram NPK per weight rather than gram per volume as given here. The relevant values were converted using a density of 1.0 g/ml. For five representatively chosen samples, densities were determined to 992 ± 6, 1000 ± 20, 1001 ± 3, 1004 ± 3, and 1010 ± 4 g/l, respectively, which verifies the assumption. For the dry matter contents, laboratory results given in percent were likewise converted to gram per liter. Figure S1 illustrates the individual NPK laboratory results versus the mean results from all laboratories for ammonium N, organic N (obtained as total N minus ammonium N), total P, and K. Standard deviations between individual measurements and the mean of the measurements for each sample are 0.25 g/l for ammonium N, 0.19 g/l for organic N (without the NPK solutions, samples 17-20 and 37-40), 0.18 g/l for total P, and 0.16 g/l for K. Particular for phosphorus a clear increase in the deviation between individual laboratories is observed for higher phosphorus contents. This may for example be ascribed unrepresentative subsampling of a small sample volume for the individual measurements at the laboratories, when a large fraction of phosphorus is found in the inhomogenously distributed solid-state fraction of the slurries. Additionally, for phosphorus it is also noted that the deviations are significantly smaller for the NPK solutions than for animal slurries (see also Table S1), which can be ascribed the homogeneous distribution of phosphorus (dissolved phosphate) in these samples. From one of the external laboratories, additional analysis of all samples were obtained for magnesium (up to 0.6 g/l), calcium (up to 4.3 g/l), sulfur (up to 0.5 g/l), copper (up to

0.028 g/l), zinc (up to 0.10 g/l), iron (up to 0.18 g/l), and nitrate N (up to 0.014 g/l). The latter confirms that no significant contents of nitrate are present in the slurries relative to the ammonium contents.

Correlations between organic N, dry matter, and NMR analysis

For the animal slurries used in the correlation study (sample 1-16 and 21-36 in Table S1), a correlation between the dry matter and organic N contents is observed as illustrated in Figure S2 based on the laboratory analysis. We note again that the content of organic N is calculated as the total N content minus the ammonium N content. Hereby, the content of organic N may be monitored by analysis of the water content (expressed as 100% minus the dry matter content) which may be obtained directly from ^{17}O NMR measurements as described in the main text.

As an alternative method, we furthermore suggest ^{13}C NMR measurements which will most likely also correlate to the organic N fraction (since the ratio between carbon and organic N is roughly constant). Attempts to demonstrate this correlation were however postponed due to a large background signal from the coil support made of Teflon and the applied sample tubes made of perfluoroalkoxy alkane (PFA). Ideally, ^{17}O and ^{13}C NMR analysis may be combined to obtain the most accurate results for organic N (and dry matter).

Detailed description of the NMR experiments and measurements at multiple NMR sensors:

As described in the main text, all NMR experiments were conducted at a static magnetic field of 1.5 T corresponding to resonance frequencies of approximately 4.6 MHz for ^{14}N, 8.7 MHz for ^{17}O, 26.0 MHz

for ^{31}P, and 3.0 MHz for ^{39}K. The ^{14}N NMR experiments of all samples at all sensors were conducted using pulse lengths of 40 μs for both π/2 and π pulses (with rf field strengths of 6.25 and 12.5 kHz, respectively), acquisition of 50 echoes separated by 400 μs, and recycle delays of 250 ms (1800 scans), 500 ms (1080 scans), 1000 ms (720 scans), and 1500 ms (360 scans) implying 3960 scans in total per sample. ^{17}O NMR experiments of the 32 slurry samples (NPK solutions not included) were conducted using pulse lengths of 25 μs for both π/2 and π pulses (rf field strengths of 10 and 20 kHz), acquisition of 24 echoes separated by 180 μs, and recycle delays of 50 ms (11200 scans), 75 ms (22400 scans), and 100 ms (5600 scans) implying 39200 scans in total per sample. ^{31}P NMR experiments of all samples were conducted using pulse lengths of 8 μs for both π/2 and π pulses (rf field strengths of 31.25 and 62.5 kHz), acquisition of 15 echoes separated by 100 μs, and recycle delays of 300 ms (2250 scans), 500 ms (1350 scans), 700 ms (1350 scans), and 900 ms (900 scans) implying 5850 scans in total per sample. ^{39}K NMR experiments of all samples at six sensors were conducted using 50 μs pulses (rf field strengths of 5 and 10 kHz), acquisition of 30 echoes separated by 440 μs, and recycle delays of 30 ms (14400 scans), 60 ms (9000 scans), 90 ms (7200 scans), and 120 ms (5400 scans) implying 36000 scans in total per sample. For the present demonstration results, the prototype NMR sensors were tuned manually between measurements of different nuclei. The echo trains showed as examples in Fig. 2 in the main text (and applied for the results in Fig. 3 in the main text) were acquired with the parameters given above and with the acquisitions added independently of the recycle delays to give a total experiment time of about 1 h for each echo train. The shown echo trains in Fig. 2 are acquired of sample 8 for ^{14}N, sample 4 for ^{17}O, sample 8 for ^{31}P, and sample 17 for ^{39}K.

The ^{14}N and ^{39}K NMR experiments were performed using six NMR sensors to ensure and demonstrate the reproducibility of the instrument. The results were calibrated for each sensor based on the

laboratory results, and the correlations of the mean values versus the laboratory results is shown in Fig. 3 in the main text. Figure S3 shows the induvidual ^{14}N and ^{39}K NMR results of the measurements performed at multiple NMR sensors plotted against the mean of the results (as also shown in Figs. 3a+d in the main text). A good agreement between the results at individual sensors is observed, and the standard deviations are 0.13 g/l for ammonium N (five sensors) and 0.36 g/l for K (six sensors). For ammonium N the results of one outlying sensor were excluded since this sensor showed instability and larger probe ringing than for the other five sensors. Including the results of the outlying sensor the standard deviation is 0.20 g/l for all six sensors.

To estimate the precision of short-term evaluation, the NMR data were acquired and stored in six to nine single blocks for each sample (six blocks of 660 total scans each for ^{14}N, eight blocks of 4900 total scans each for ^{17}O, nine blocks of 650 total scans each for ^{31}P, and six blocks of 6000 total scans each for ^{39}K). Each of these blocks were stored in four subblocks acquired using four different recycle delays, which may be accumulated directly or utilized for extraction of information on T_1 relaxation times. While the results for all blocks (for each of the four nuclei) including extensive data and experiment processing were acquired over 1 h for each sample, the effective experiment duration per sample was 39 min for ^{14}N, 49 min for ^{17}O, 52 min for ^{31}P, and 46 min for ^{39}K. For online measurements exploiting the full detection volume of diameter 9.2 mm, the number of examined spins and thus the sensitivity is increased with a factor of 1.32 relative to the demonstrations with 8 mm inner diameter of the removable sample containing tubes. This implies that one examination block (composed of four subblocks with different recycle delays) corresponds for in-line measurements to a measuring time of 3.7 min for ^{14}N, 3.5 min for ^{17}O, 3.3 min for ^{31}P, and 4.4 min for ^{39}K, or up to about 5 min for each when time for regular data and experiment processing is allowed. For the processing

algorithm applied for the ammonium-N data shown in Fig. 3a, a precision of 0.23 g/l in standard deviation is obtained for evaluation of the 1200 acquired blocks (for five ^{14}N sensors) corresponding to 3.7 min in-line measurements. For oxygen the standard deviation on single block (3.5 min) evaluation of organic N is 0.27 g/l (based on 320 measurements on a single ^{17}O sensor). For phosphorus, it is 0.20 g/l for 3.3 min measurements (based on 360 measurements on a single ^{31}P sensor), and for potassium (4.4 min evaluations) it is 0.76 g/l based on 1440 measurements from the six applied ^{39}K sensors. These deviations on short term measurements are similar to the obtained deviations relative to laboratory reference measurements, and short term measurements are suitable for practical applications with measuring times of about 5 minutes. In all cases, further accelerated estimates of nutrient contents are available in compromise with the detection uncertainty. For the ^{14}N evaluation of ammonium N for example, the standard deviation determined above will theoretically increase to 0.5 g/l for 1-min evaluations and to 1 g/l for rapid evaluations of 15 s.

The ^{31}P measurements were initially also performed using six NMR sensors with a 10 cm long coil as for the other nuclei and with rf pulses with durations of 12 μs (rf amplitudes of 21 and 42 kHz for $\pi/2$ and π pulses, respectively). These experiments showed unclear results due to sample-dependent variation of the quality factor and return loss of the probes and due to floculation of the sample in the sample tubes. However, the initial results showed excellent agreement of the results of individuals sensors with a standard deviation of approximately 0.09 g/l on the results of analysis for six NMR sensors.

Tables

Table S1: Overview of the samples with description of sample type as well as analysis results (mean value with standard deviations) from five commercial laboratories. Laboratory results are shown for dry matter, ammonium nitrogen, total nitrogen, total phosphorus, potassium, pH (we note that pH was only analyzed at four laboratories for sample 1-20 and only three laboratories for sample 21--40). Slurry samples 21-36 are duplicates of sample 1-16 with randomized sample numbers, and duplicate samples are listed together (e.g., samples 1 and 24). Samples 17-20 and 37-40 are NPK solutions, of which samples 38, 40, 19, and 20 are dilutions of samples 17, 18, 39, and 37, respectively. Samples 21-40 were analyzed at the laboratories approximately three weeks later than samples 1-20. For dry matter of samples 7, 10, and 11, reported values <5 g/l from one laboratory were omitted as outliers.

Sample number	Description	Dry matter (g/l)	NH_4^+ N (g/l)	Total N (g/l)	Total P (g/l)	K (g/l)	pH
1	Pig slurry	39 ± 3.8	2.5 ± 0.15	4.0 ± 0.37	0.8 ± 0.16	2.0 ± 0.15	6.2 ± 0.09
24		38 ± 4.4	2.6 ± 0.18	3.9 ± 0.10	0.8 ± 0.11	2.0 ± 0.14	6.2 ± 0.05
2	Pig slurry	33 ± 1.5	2.5 ± 0.17	3.4 ± 0.06	0.6 ± 0.13	2.2 ± 0.15	7.0 ± 0.06
34		33 ± 2.6	2.5 ± 0.16	3.5 ± 0.11	0.6 ± 0.12	2.1 ± 0.14	6.8 ± 0.05
3	Pig slurry	15 ± 2.2	2.3 ± 0.09	2.8 ± 0.13	0.1 ± 0.02	2.5 ± 0.15	7.5 ± 0.10
25		16 ± 0.5	2.3 ± 0.15	2.9 ± 0.16	0.1 ± 0.02	2.5 ± 0.15	7.6 ± 0.05
4	Pig slurry	43 ± 6.6	1.9 ± 0.19	3.1 ± 0.08	2.4 ± 0.58	1.3 ± 0.05	7.6 ± 0.16
33		46 ± 9.3	2.0 ± 0.18	3.2 ± 0.13	2.2 ± 0.88	1.3 ± 0.06	7.6 ± 0.05
5	Mink slurry	34 ± 2.0	2.9 ± 0.20	4.4 ± 0.13	1.4 ± 0.24	0.5 ± 0.07	7.0 ± 0.08
28		34 ± 1.1	3.0 ± 0.23	4.5 ± 0.18	1.4 ± 0.16	0.6 ± 0.04	7.0 ± 0.09
6	Digested slurry (mainly pig)	8 ± 1.2	1.8 ± 0.08	2.2 ± 0.07	0.1 ± 0.05	1.4 ± 0.12	7.8 ± 0.11
23		9 ± 1.0	1.8 ± 0.09	2.2 ± 0.08	0.1 ± 0.02	1.5 ± 0.11	7.8 ± 0.10
7	Cattle slurry	40 ± 1.8	1.4 ± 0.12	2.6 ± 0.02	0.5 ± 0.07	2.4 ± 0.22	7.3 ± 0.10
27		40 ± 1.7	1.4 ± 0.13	2.6 ± 0.14	0.5 ± 0.04	2.4 ± 0.17	7.3 ± 0.15

8	Mink slurry	33 ± 3.3	4.4 ± 0.65	6.0 ± 0.07	1.8 ± 0.33	0.8 ± 0.20	7.0 ± 0.07
21		34 ± 3.1	4.6 ± 0.30	6.0 ± 0.09	1.8 ± 0.30	0.8 ± 0.06	7.0 ± 0.06
9	Mink slurry	2 ± 0.8	0.3 ± 0.11	0.4 ± 0.16	0.1 ± 0.05	0.2 ± 0.14	7.1 ± 0.14
26		4 ± 4.2	0.3 ± 0.09	0.5 ± 0.26	0.1 ± 0.02	0.2 ± 0.14	7.1 ± 0.08
10	Pig slurry	14 ± 2.4	2.4 ± 0.13	3.0 ± 0.07	0.2 ± 0.04	1.9 ± 0.15	7.6 ± 0.20
36		15 ± 0.8	2.5 ± 0.14	3.2 ± 0.18	0.2 ± 0.04	1.9 ± 0.12	7.7 ± 0.07
11	Cattle slurry	33 ± 1.8	0.8 ± 0.08	1.7 ± 0.09	0.3 ± 0.03	1.6 ± 0.11	7.2 ± 0.11
30		34 ± 1.1	0.8 ± 0.09	1.8 ± 0.22	0.3 ± 0.02	1.6 ± 0.11	7.3 ± 0.15
12	Cattle slurry	93 ± 3.2	2.0 ± 0.18	4.4 ± 0.08	0.7 ± 0.07	3.9 ± 0.37	6.7 ± 0.07
35		94 ± 1.9	2.1 ± 0.24	4.4 ± 0.08	0.8 ± 0.06	3.9 ± 0.24	6.6 ± 0.07
13	Digested slurry (mixed)	53 ± 3.2	1.5 ± 0.10	3.0 ± 0.17	0.5 ± 0.04	2.4 ± 0.18	7.8 ± 0.06
31		52 ± 3.0	1.5 ± 0.13	2.9 ± 0.10	0.4 ± 0.09	2.4 ± 0.13	7.8 ± 0.06
14	Cattle slurry	64 ± 4.4	1.3 ± 0.10	3.0 ± 0.22	0.5 ± 0.06	2.5 ± 0.19	7.2 ± 0.09
22		64 ± 1.7	1.4 ± 0.16	2.9 ± 0.16	0.6 ± 0.06	2.5 ± 0.15	7.1 ± 0.05
15	Cattle slurry	67 ± 2.6	1.8 ± 0.14	3.6 ± 0.15	0.7 ± 0.05	2.5 ± 0.19	7.3 ± 0.08
32		67 ± 0.6	1.8 ± 0.18	3.5 ± 0.08	0.7 ± 0.03	2.5 ± 0.07	7.3 ± 0.15
16	Digested slurry (mainly cattle)	58 ± 2.0	1.6 ± 0.13	3.2 ± 0.18	0.5 ± 0.06	2.7 ± 0.22	7.9 ± 0.11
29		57 ± 2.0	1.7 ± 0.17	3.1 ± 0.09	0.5 ± 0.05	2.7 ± 0.16	7.9 ± 0.06
17	NPK solution	44 ± 2.7	6.8 ± 0.98	7.3 ± 0.35	2.3 ± 0.13	8.9 ± 0.41	7.0 ± 0.05
38	63.5% sample 17	27 ± 2.5	4.4 ± 0.26	4.8 ± 0.30	1.5 ± 0.09	5.5 ± 0.32	7.0 ± 0.02
18	NPK solution	54 ± 5.9	14.1 ± 0.84	14.9 ± 1.70	1.3 ± 0.12	3.1 ± 0.23	7.2 ± 0.09
40	50% sample 18	27 ± 5.7	6.9 ± 0.23	7.2 ± 0.27	0.7 ± 0.04	1.6 ± 0.08	7.2 ± 0.11
19	50% sample 39	14 ± 1.8	2.6 ± 0.15	2.9 ± 0.22	0.4 ± 0.03	2.8 ± 0.09	7.4 ± 0.08
39	NPK solution	27 ± 3.4	5.1 ± 0.21	5.6 ± 0.34	0.8 ± 0.05	5.4 ± 0.23	7.3 ± 0.11
20	42% sample 37	3 ± 1.9	0.9 ± 0.08	1.1 ± 0.11	0.2 ± 0.05	0.6 ± 0.13	5.5 ± 0.06
37	NPK solution	10 ± 2.2	2.2 ± 0.17	2.5 ± 0.36	0.4 ± 0.03	1.5 ± 0.10	5.4 ± 0.06

Figures

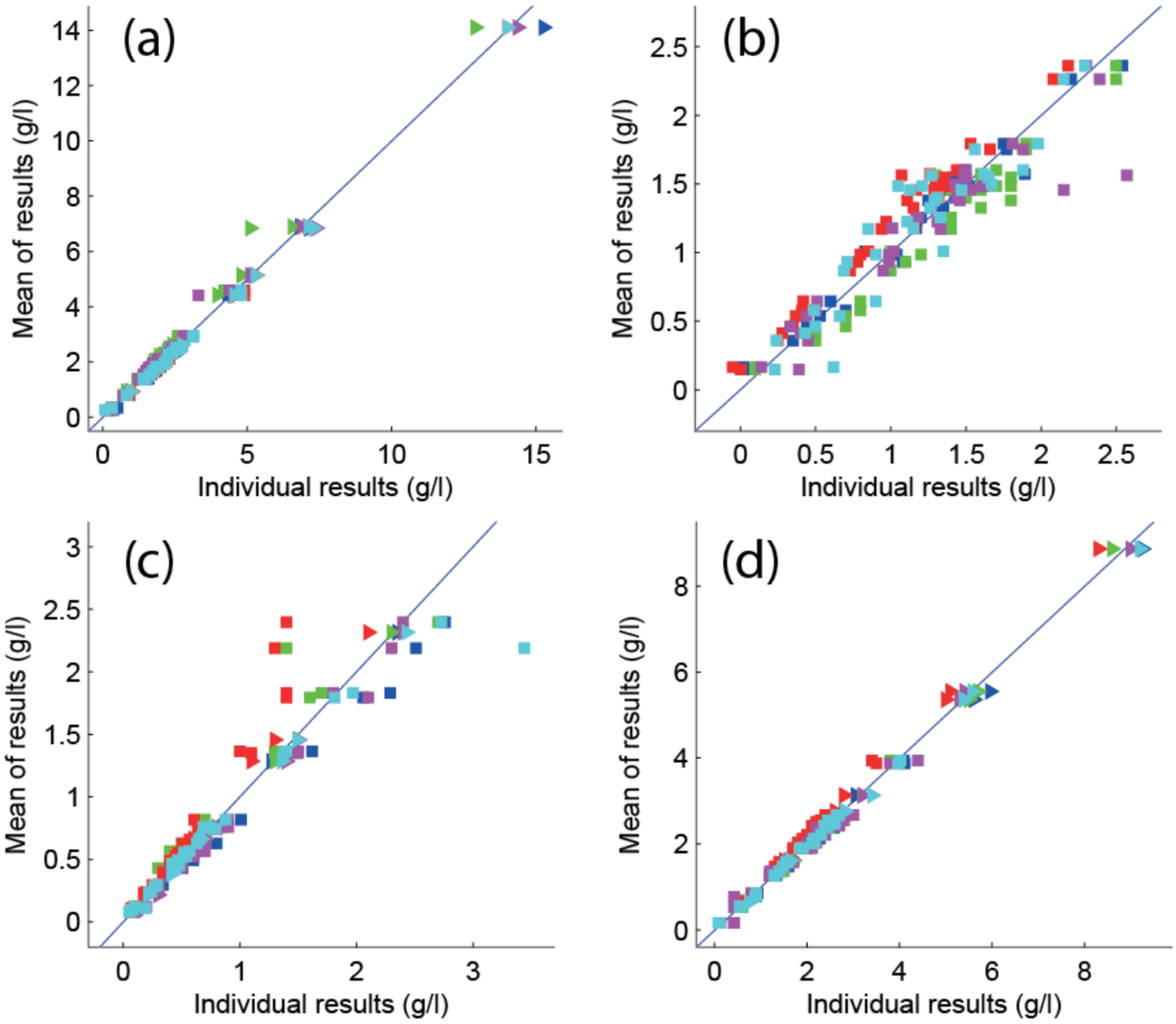

Figure S1: Individual laboratory results plotted versus mean of the laboratory results for (a) ammonium nitrogen, (b) organic nitrogen obtained as total N minus ammonium N, for which only the 32 slurry samples (samples 1-16 and 21-36) are included, (c) total phosphorus, and (d) potassium. The five different colors of the marks represent the five different external laboratories. Squares represent

slurry samples (samples 1-16 and 21-36) whereas triangles represent NPK solutions (samples 17-20 and 37-40).

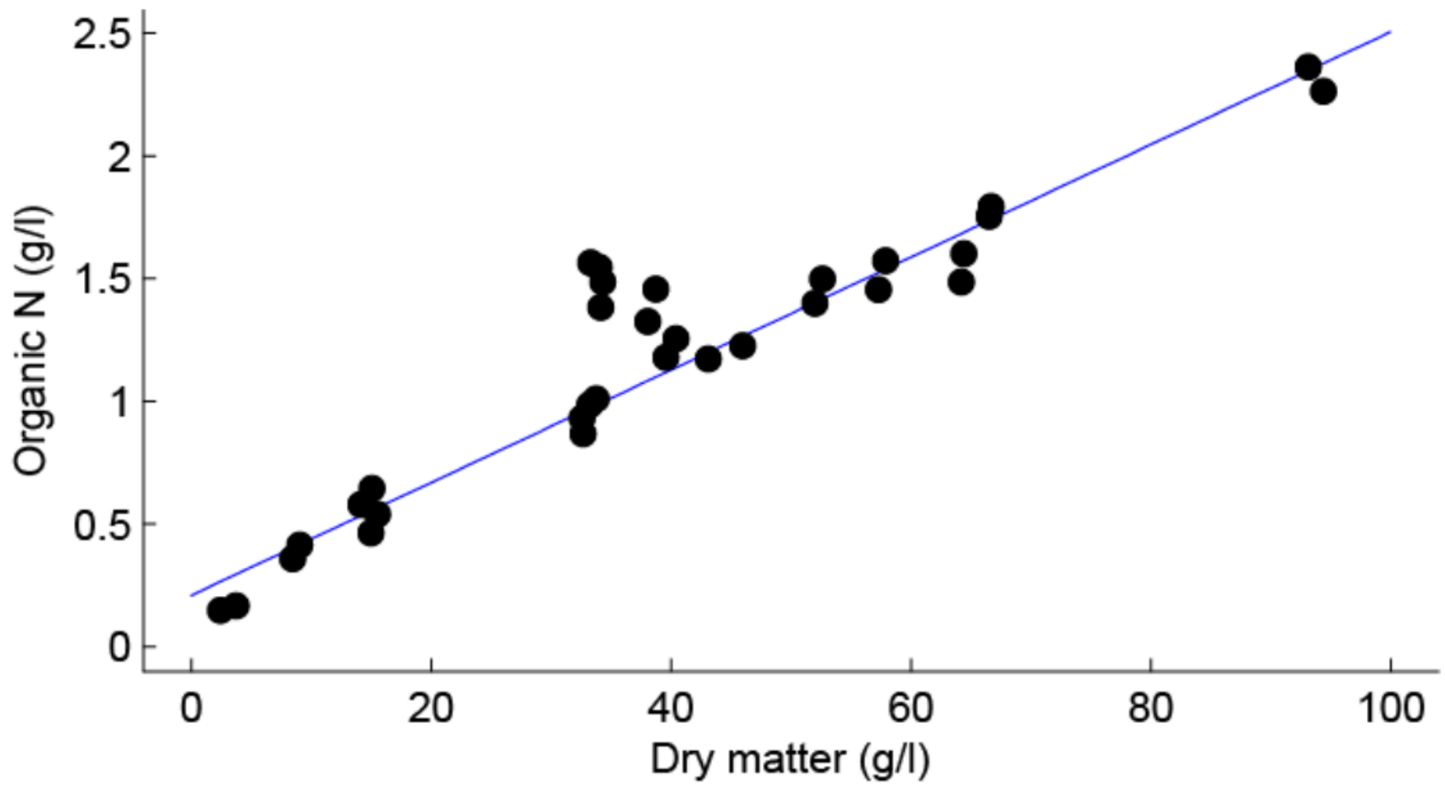

Figure S2: Organic N (total N minus ammonium N) versus dry matter contents based on mean laboratory results for each of the slurry samples (1-16 and 21-36). Results of duplicate samples are observed close to each other for all 16 different slurries (see Table S1 for precise numbers). For the mink slurries the organic N contents are seen to deviate with up to 0.6 g/l from the linear correlation to dry matter indicated with the straight line.

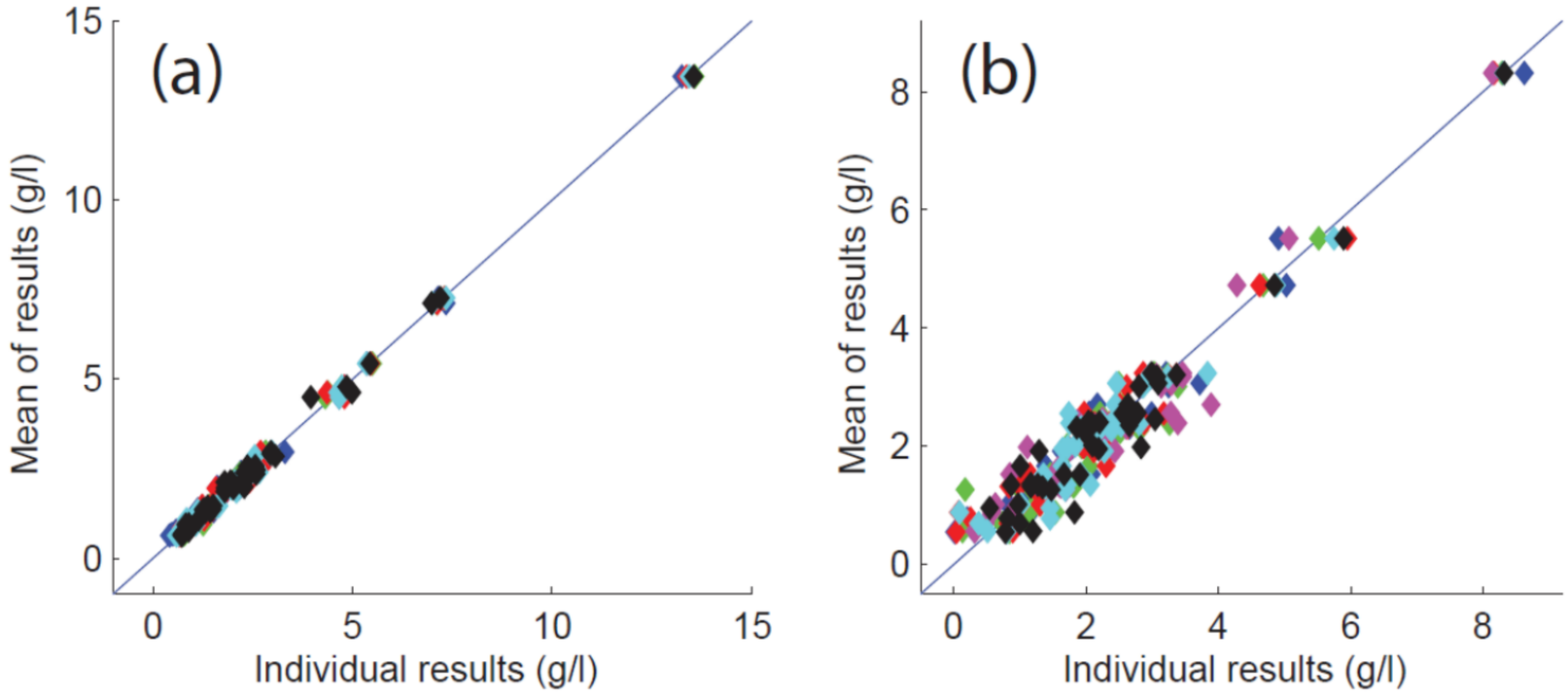

Figure S3: NMR results of individual sensors versus the mean results for (a) the ammonium-N contents measured at five ^{14}N NMR sensors and (b) the K contents measured at six ^{39}K NMR sensors, and with parameters as described in the text. Each color represents a different NMR sensor.