

MAP Program

Proficiency Report 2010 Round 2

Robert O. Miller, PhD., Colorado State Univ. Fort Collins, CO



2010 Round 2

The MAP 2010 Round 2 had sixty-five of sixty-six labs enrolled provide results. Samples were prepared by Jerry Floren of the Minnesota Dept of Agriculture, Saint Paul, MN. Samples **M-10D** (sub-samples 56, 61, and 62) is a liquid material (replicated as M-10-A), **M-10E** (sub-samples 57, 59 and 64) was caged chicken litter and **M-10F** (sub-samples 58, 60 and 63) was turkey litter with bedding.



Special points of interest:

- Median Total Solids for the three materials ranged from 3.3 to 74.0%.
- TKN results ranged from 0.106 % to 2.375 % for the three samples.
- SO₄ intra-lab precision was excellent averaging 0.8% across the three samples.
- Total K results ranged from 0.145 to 1.91 % for the three samples.
- The MAP 2010 Round 2 median laboratory proficiency score was 89.5% and the precision score was 92.9%.

Methods evaluated in the MAP program are based on those listed in *Recommended Methods of Manure Analysis* edited by John Peters (<http://cecommerce.uwex.edu/pdfs/A3769.PDF>) and include: total solids, electrical conductivity (EC, 3 methods), pH, NH₄-N (3 methods), NO₃-N, SO₄-S, Cl, TKN-N, combustion nitrogen, phosphorus, potassium, calcium, magnesium, sodium, sulfur, zinc and copper.

The data report for 2010 is listed by analysis with subheadings by sample. Outlier values exceeding $\pm 4.0 \times \text{MAD}$ were removed and Confidence Limits (CL) based on 95% of the median were compiled. The lab data report statistics include: the number results, minimum value, maximum value, median value, confidence limits, overall reproducibility (*R_d*), individual reported lab values, repeatability (*R_p*) of lab value; and mean lab value reported. Lab proficiency, 95% CL, are based on the median $\pm 2.9 \times \text{MAD}$ and bias is flagged as ***L** or ***H**. Lab precision is based on *R_p* values exceeding three (3) times the *R_d*, and are flagged with a ***P** adjacent to the *R_p* results.

Inside this issue:

Results	1
Ammonium Analysis	3
Potassium Results	3
Replicated Sample Comparison	4
Proficiency and Precision Scores	4

Results

Total solids were reported by 61 labs with median values ranging from 3.3 - 74.0%, with confidence limits (CL) ranging from ± 0.96 to ± 2.6 percent total solids across the three samples. Intra-lab reproducibility (*R_d*) values ranged from 0.4 to 4.1 % across the three materials, increasing with decreasing total solid content.

EC (1:1) analysis was completed by 12 laboratories and 27 for EC 1:2. Median CL for EC (1:2) concentrations ranged from $1.7 \pm 0.20 \text{ dSm}^{-1}$ to $13.4 \pm 5.0 \text{ dS/m}$, highest for sample **M-10E**. Manure pH was reported by 43 labs, with values ranging from 7.16 to 7.86. Nitrate across samples median concentrations ranged from 1.7 to 394 mg kg⁻¹, with confidence limits ranging from ± 3.5 to ± 313 of the median.

Results (Continued)



For 2010 was the addition of EC 1:5 median concentrations ranged from 0.9 to 5.3 dSm⁻¹ with confidence limits ranging from 0.2 to 3.3 dSm⁻¹ with an average of 30 labs reporting. *Rd* values ranged from 1.7 to 2.9 %.

MAP 2010 NH₄-N values are reported as % on as received basis. NH₄-N analysis was separated into three methods: ISE (ion selective electrode); spectrophotometric (SPEC); and distillation. Three labs provided results for the ISE method, 20 for SPEC and 32 for distillation. NH₄-N median concentrations for the Distillation NH₄-N median concentrations ranged from 0.007 % to 0.700 %. Generally confidence limits were the narrowest for SPEC method, averaging ± 0.115 % NH₄-N. *Rd* values for the distillation method averaged 1.6 % for the two of the three materials, while the SPEC method ranged from 1.3% - 4.9%, and the ISE method ranged from 1.3% - 4.9%.

Total Kjeldahl Nitrogen (TKN) median concentrations for the three samples ranged from 0.106 % to 2.375 % with confidence limits of ± 0.058, ± 0.218 and ± 0.168 percent nitrogen, respectively. TKN intra-lab *Rd* values averaged 1.5 % for the two highest materials. Total Nitrogen (by the Dumas combustion - TN) was reported by an average of 34 labs resulted in median values approximately 0.140 % higher than the TKN on sample **M-10F**. Confidence limits for TN were 1.3 times higher than the TKN method for **M-10D** and **M-10E**. *Rd* values for TN were 7.8 %, 1.8 %, 2.2 %, respectively.

Fifty-eight labs provided total phosphorus (P) and potassium (K) with median sample concentrations ranging from 0.031 to 1.718 % P and 0.145 to 1.910 % K. Confidence Limits (CL) ranged from ± 0.011 to ± 0.227 percent P. Intra-lab *Rd* P values averaged 2.5 % for two of the three materials indicating good intra-lab precision for the method. For K CL ranged from ± 0.023 to ± 0.238 percent K. *Rd* values for K averaged 2.2% for the three materials indicating good intra-lab precision for the method.

Water Extractable Phosphorus (WEP) was provided by twelve labs. Sample median values ranged from 2490 to 6690 mg/kg with confidence limits approaching 60 % of the median. *Rd* values averaged 3.2 %.

Median sulfur (S) values ranged from 0.024 % to 0.607 % with confidence limits ranging from ± 0.009 to ± 0.186 percent S. *Rd* values for S ranged from 2.1% to 4.7% across the three samples. Calcium (Ca) and Magnesium (Mg) was reported by 49 labs. Na results were provided by an average of 46 labs with median values ranging from 0.010 % to 0.357 % Na. An average of 51 labs provided zinc (Zn) results and 50 copper (Cu). Across samples median Zn concentrations ranged from 5.5 to 312 mg kg⁻¹ with confidence limits of ± 45 mg kg⁻¹ for samples **M-10F**. Median Cu values ranged from 1.10 to 86.7 mg kg⁻¹ with confidence limits averaging ± 7.1 mg kg⁻¹ for samples **M-10E**. *Rd* values for Zn and Cu ranged from 2.2 % to 9.5 %, with the lowest values noted for sample **M-10E**.

“TKN Intra-lab Rd values averaged 1.5% for two of the three materials”



Ammonium Analysis

Ammonium (NH₄-N) analysis of manure in the MAP program is evaluated by three methods: Ion Selective Electrode (ISE), spectrophotometric (SPEC) and distillation. For MAP 2010 three labs provided results for ISE, twenty labs for the SPEC method and thirty-two labs for Distillation. Results for MAP **M-10E** indicates results for the ISE and SPEC methods to be similar and not statistically different. Whereas results for Distillation is significantly higher than the other two methods. Similar differences were noted for samples **M-10D** a liquid manure sample.

Across MAP samples utilized since 2004 it has been noted that the Distillation method has a consistent high bias relative to the ISE and SPEC methods. The differences are associated with the method of ammonium extraction noted in *Recommended Methods of Manure Analysis*. The SPEC method is based on extraction with KCl with subsequent SPEC determination. Distillation method bias is likely associated with sodium hydroxide liberation of NH₄-N and organic amines in the manure resulting in the high relative bias.

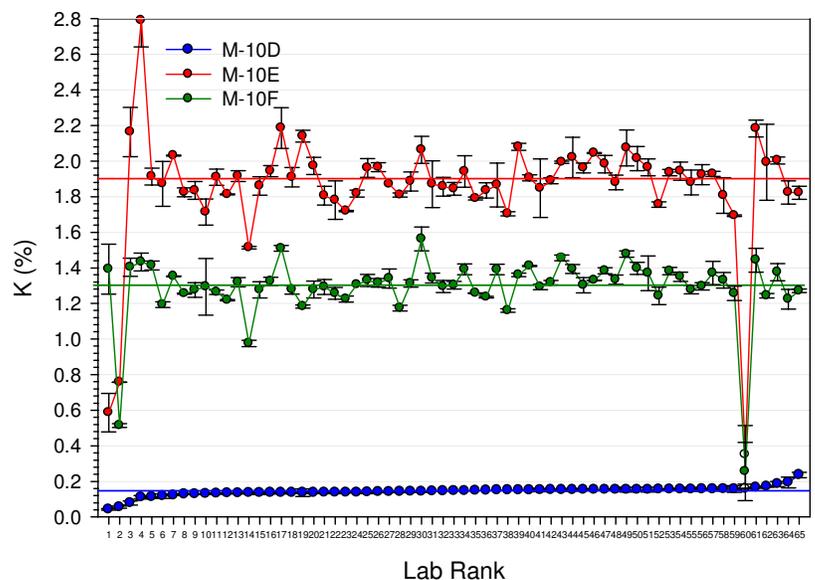
Table 1. MAP Ammonium results M-10E

	Median	± CL
	%	
ISE	0.310	0.174
SPEC	0.239	0.107
Distillation	0.447	0.052

Potassium Results

Total potassium (K) sample results for the MAP 2010 Round 2 indicate a range in median values, of 0.145, 1.910 and 1.311 % total K, across the three manure samples respectively. This is best illustrated in Figure 1, which plots individual lab results ranked from low to high, based on MAP sample **M-10D**. Listed is the median, standard deviation error bars for each manure sample material. Sample **M-10D**, indicates three labs exceeding a CL of ± 0.023 % K, two with low bias relative to the median. Sample **M-10E**, had a narrow distribution in total K values ranging from 0.160 to 2.96 % K, with four labs results exceeding confidence limit of ± 0.238 % total K. Sample **M-10E** shows a distribution in K values ranging from 0.160 to 1.62 % total K, again resulting in two labs exceeding a confidence limit of ± 0.157 % total K. Generally standard deviation error bars across labs were highest for sample **M-10E**, and the lowest for sample **M-10D**. Across the three samples lab #3 had a consistent high bias across two of the three manure materials. Lab #60 and #2 had inconsistent results, indicating a bias trend high on one of three materials. Lastly, across samples, lab #1 had the largest error bars across all three manure samples, whereas lab # 24 had the lowest error bars.

Figure 1. K Distribution for MAP 2010 RD2.





**JERRY FLOREN
MINNESOTA DEPT OF
AGRICULTURE**

Phone: 651-201-6642
Fax: 651-201-6117
Email: jerry.floren@state.mn.us

**ROBERT O. MILLER, PHD.,
COLORADO STATE UNIV. FORT
COLLINS, CO**

Phone: 970-686-5702
Fax: 970-686-5709
Email: rmiller@amar.colostate.edu

**Renew for
2011**

Replicate Sample Comparison

MAP sample **M-10D** was a replicate of sample **M-10A** used in Round 1 of 2010. Results indicate nearly identical median values for total Solids, TKN, P and K values (see Table 2), with difference often noted only at the 3rd significant digit. For total P and K Confidence Limits (CL) values were lower for the **M-10D** than **M-10A**. *Rd* values ranged were in general lower for sample **M-10D**. In conclusion these results show very high agreement in analytical values for a manure sampled duplicated through the course of a year across 65 testing laboratories.

Table 2. Comparison of sample results.

Sample	M-10A			M-10D		
	Median	± CL	Rd (%)	Median	± CL	Rd (%)
Total Solids	3.24	0.73	5.7	3.27	0.96	4.1
TKN	0.102	0.050	6.1	0.106	0.058	5.3
Total P	0.032	0.016	6.5	0.031	0.011	7.8
Total K	0.143	0.029	2.9	0.145	0.023	2.3

Proficiency and Precision Scores

The MAP 2010 Round 2 median proficiency score (evaluation of bias) was 89.5% across MAP samples and methods for 65 reporting labs, an increase of 1.4% from MAP 2010 RD1. The reason for the decrease is unknown. Forty-three reporting labs had a proficiency score of more than 80%, Thirty-two a score of 90% or higher and six labs met a score of 100% (see Figure 2). Twenty-one labs had proficiency scores of less than 80%.

The median precision score was 92.9%, which was a decrease in score from 2010 RD1. Precision values are flagged based on lab *Rp* values exceeding 3 x *Rd* consensus statistics. Twenty-one labs had a 100% precision score, thirty-eight had precision scores 90% or higher.

MAP Laboratory performance information is for internal laboratory evaluation purposes only, and not for use in marketing or advertising.

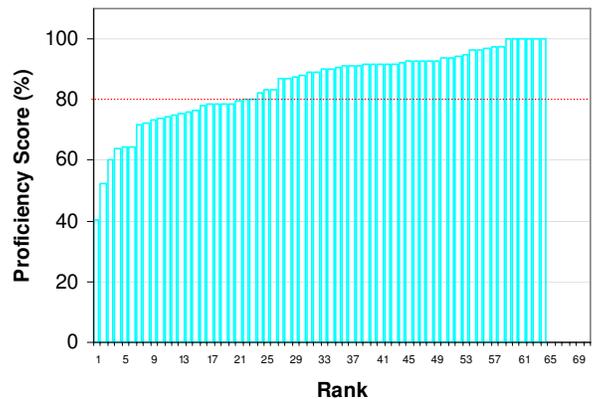


Figure 2. Proficiency Scores MAP 2010 Round 2.

*Fore more information on MAP Lab Certification
contact Jerry Floren at : Jerry.Floren@state.mn.us*