MANURE TOTAL NITROGEN VARIABILITY DUE TO ANALYTICAL METHOD AND TOTAL SOLIDS CONTENT

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ABSTRACT

Knowing the nutrient analysis of a fertilizer source is essential to ensure adequate nutrients are applied for crop growth, while not causing potential environmental impacts by overapplying nutrients. Using manure as a nutrient source can complicate matters as the nutrient content can be variable and the manure can come in a range of liquid to solid consistencies. There are multiple laboratory methods to determine different nutrient parameters and for manure total nitrogen (N) levels the most common methods are total Kjeldahl nitrogen (TKN) and nitrogen combustion (N-C). What laboratory method is the best suited for liquid or solid manure and is the least variable? The Minnesota Department of Agriculture (MDA) administers the Manure Analysis Proficiency (MAP) Program, which is the only manure proficiency program in North America where laboratories receive unknown manure samples to analyze. We used the MAP Program data back to 2003, which includes 6-9 unique sample exchanges with laboratories annually. We compared 4047 samples analyzed by the N-C method and 4536 samples analyzed by TKN method for total nitrogen. No significant difference in sample medians was found between analytical methods, however the N-C method was more variable than the TKN method for manure samples with less than 25% total solids. Being aware of the variability in these methods can help laboratories and nutrient management planners consider methods appropriate for their clients.

INTRODUCTION

When land applied, manure provides nutrients for growing crops. However, these nutrients can be variable depending on animal species, age, diet, management, housing, climate, and manure storage and handling. Knowing what nutrients are contained in a certain manure can assist farmers to better match manure application to field and crop needs. Laboratories have tested manure for many years but there was no coordinated effort for a laboratory proficiency program to ensure consistency across laboratories. Since 1996, the MDA has shipped prepared manure samples and collected data on these exchanges as a part of the MAP Program. From 2003-2006, MDA received Environmental Protection Agency (EPA) funding to create a nationwide manure proficiency program. The MDA currently continues this nationwide program and now includes Canadian laboratories as well. Laboratories participate in the MAP program to compare their laboratory's accuracy and precision to other laboratories and can become a MAP-certified laboratory annually. Laboratories receive feedback on items to improve upon and the certification process gives confidence to customers that

they are receiving quality analyses. The MAP program data allows comparison of laboratory methods across labs and years.

With many nutrient management plans using N-based manure application rates, having confidence in the total N manure test results is important. Often there are multiple analytical methods for the parameters measured. The most common TN analytical methods are TKN and N-C. For N-C, a manure sample is combusted in an oxygen-containing environment and a thermal conductivity conductor quantifies the inorganic and organic N concentrations. The TKN method uses a Kjeldahl digestion with concentrated sulfuric acid, a metal catalyst, and salts to measure the organic N and NH_4-N concentrations. TKN does not measure nitrate or nitrate levels in manure, which manure contains little of. Near-Infrared Spectroscopy (NIR) can also be used to measure total N in poultry litter but is not used as often as TKN or N-C and thus is not included in this research. The TKN and N-C methods were compared going back to 2003. TKN was the most popular TN method in 2003 and is slowly declining in popularity and today N-C is the most common TN method as indicated by Figure 1.

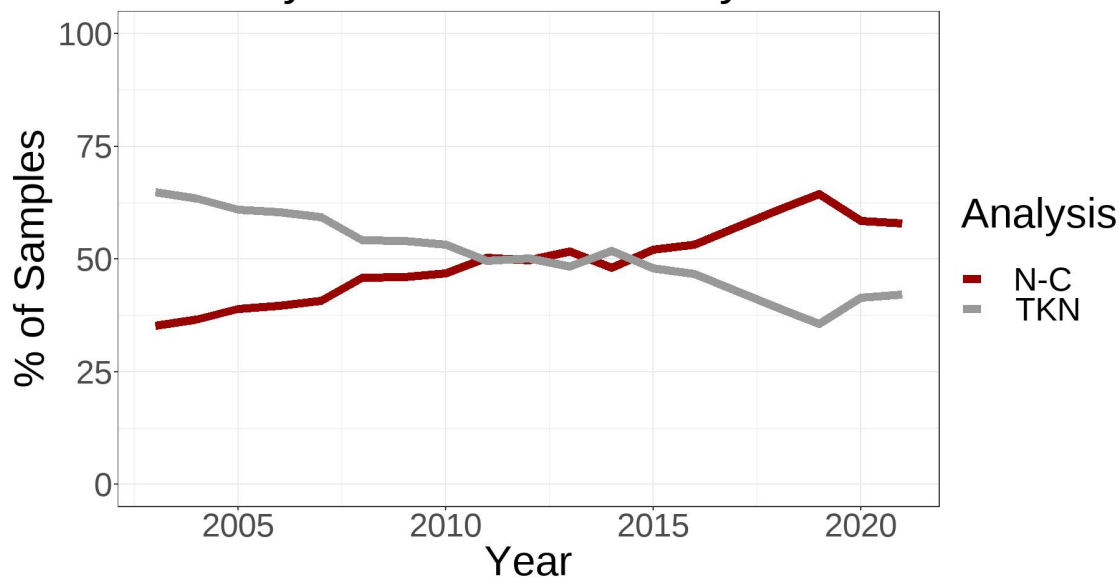## Percent of manure samples run
by N-C or TKN each year

Figure 1. Trends in total nitrogen analytical methods used from 2003-2021.

MATERIALS AND METHODS

The MAP program has sent out manure sample exchanges two to three times per year since 2003 with an annual enrollment of 60 to 74 laboratories. Each exchange contained three manure samples in triplicate, for a total of nine bottles for each laboratory to analyze. The manure samples came from different animal types and a range (2-90%) of total solids (TS). Samples were considered liquid, slurry, or semi-solid when under 20% TS in the specially prepared MAP program samples. Central Lakes College (Staples, MN) specially ground, homogenized, and packaged the manure

samples. Samples were mixed in a 60-quart Robot Coupe Vertical Cutter Mixer or in a 60-quart Robot Coupe Blixer to reduce particle size. A 12.5 cubic foot Imer cement mixer *(*Poggibonsi, Italy) mixed the solid manure samples. The exchange samples were frozen and shipped to program participants. Each laboratory submitted their analytical results on 12 test parameters on a standard template to MDA for statistical analysis.

This study compared 120 unique manure samples from 2003-2021 minus 2017 between the N-C to TKN methods. The 2017 data was not included as the MAP Program tried an experimental exchange method using 15 samples of freeze-dried manure with no replicates. The R programming language was used for statistical analysis (R Core Team, 2022). We calculated the lab mean for the triplicate samples, and then found the median for each sample across all labs for the TKN and N-C method each. We compared the medians values for the TKN and N-C samples using the unpaired (independent samples) t-test. We used median absolute deviation (MAD) to analyze the spread of the data without having exceptionally high or low values skew the results. MAD is calculated by finding the median of a data set, subtracting the median from each value in the dataset, and then finding the median from those calculations. Like a coefficient of variation, a Relative Median Deviation (RMD) is a dimensionless number that would indicate method precision in this case and is calculated by dividing the MAD by the median and multiplying by 100. Unpaired t-tests compared the RMDs between the two methods. The samples were divided into separate categories by TS percentages and RMDs were compared by method.

RESULTS AND DISCUSSION

The TKN and N-C sample TN% medians were not significantly different and the violin plots in Figure 2 show those median comparisons. When comparing the TN RMDs vs TS, there was not a significant difference between the precision of the two methods overall. However, when divided between distinct levels of TS, the RMDs were significantly different between TN methods for the manure samples with less than 25% TS, with the N-C having less precision compared to TKN for those samples. Figure 3 shows the TN RMDs compared to TS. The MAP Program helps minimize manure test variability and past MAP samples can answer some questions regarding method choice. Overall either method is still a recommended option for TN analysis and both are listed in the recently updated book, <u>Recommended methods of manure analysis 2nd edition</u> (Wilson & Cortus, 2022). Understanding there is some precision variability with samples with less solids can help laboratories and nutrient management planners consider methods appropriate to their clients.

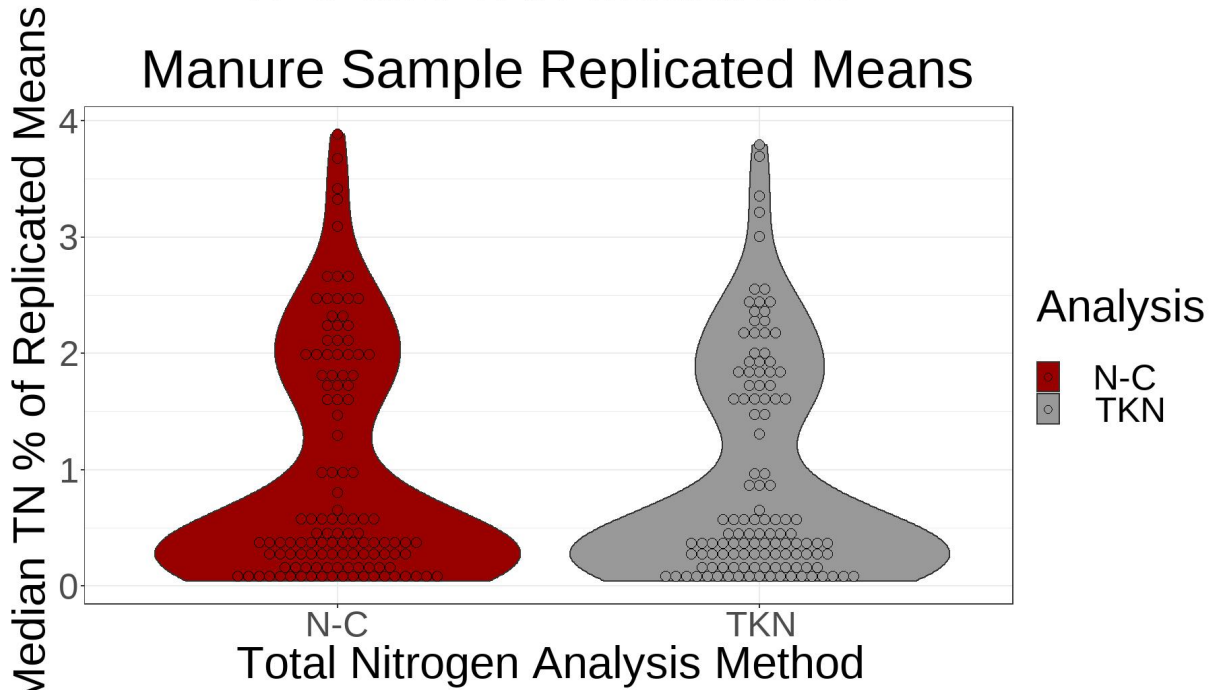# N-C and TKN Medians of

Manure Sample Replicated Means

Figure 2. The N-C and TKN medians of replicated manure samples are not significantly different from each other.
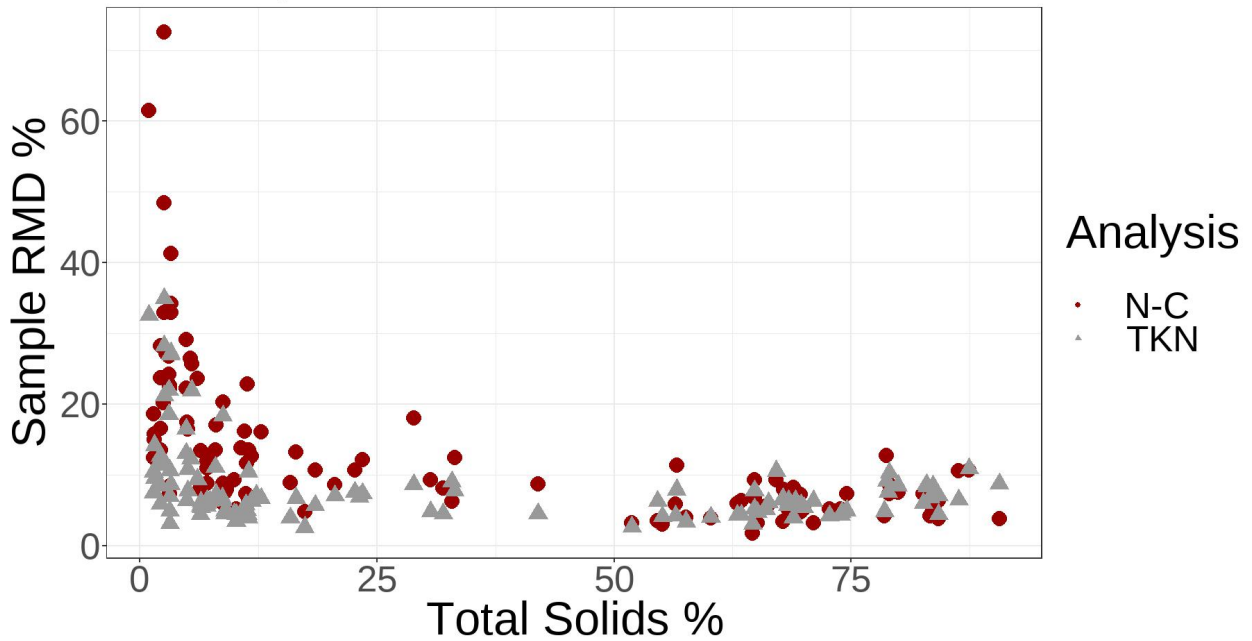
N-C and TKN RMDs

compared to Manure Total Solids

Figure 3. The RMDs are significantly different between methods when total solids are less than 25%.

ACKNOWLEDGEMENT

REFERENCES

R Core Team. (2022). *R: A Language and Environment for Statistical Computing*. R
    Foundation for Statistical Computing. https://www.R-project.org/
Wilson, M. L., & Cortus, S. (Eds.). (2022). *Recommended methods of manure analysis*
    (Second edition). University of Minnesota Libraries Publishing.