Abstract

Animal manures are a significant resource for agricultural crop production throughout the world. Producers apply manure to meet the needs of the crops that they plan to grow, while reducing the negative impact that excess applications can have on the environment. Predicting the availability of the nitrogen (N) within the manure would help producers determine their desired manure application rates with greater accuracy. The first step to predicting N availability is determining the carbon to nitrogen (C:N) ratio. The problem with determining the actual C:N ratio is that the procedure is too expensive for most practical purposes. Using the Elementar vario MAX CN Analyzer in the University of Wisconsin Soils Lab, we determined the actual C:N ratio of various types of manure and compared the results with those of the routine procedures used by the University of Wisconsin Soil and Forage Analysis Lab. We found that while the routine tests could not accurately predict the actual percentage of carbon in the manure, the procedures could predict the actual C:N ratio. With future research on the relationship between C:N ratio and N availability of manure, this data could be used to assist producers with their manure management practices without having to pay for extra testing procedures.

Introduction

Application of manure to land used for agricultural production is a long standing practice within the state of Wisconsin, as well as around the world. The manure provides important nutrients to the crops that are to be grown and additionally improves the overall condition of the soil. Organic soil amendments such as manure improve soil tilth, microorganism activity and increase organic matter content. Animal manures are especially abundant in areas of high livestock production, Wisconsin being no exception. Dairy, beef, pork and poultry producers always have a supply of manure to apply to their crop fields. Sometimes the supply is so great that it is a challenge to properly manage the application of the animal waste. Many environmental issues arise with the careless and
over application of crop nutrients, especially manure. Manure applications can result in groundwater and surface water contamination. In serious cases fish kills can occur.

Regardless of problems that arise, the benefits of using manure as a fertilizer are a great asset to producers. This is especially true with today’s increasing synthetic fertilizer prices. At 50 cents or more per pound of nitrogen, growers need to use their resources wisely. The economics of crop production, along with the environmental concerns of manure applications, emphasize the importance of efficient nutrient management practices.

However, efficient manure application is hard to achieve because of the variability that exists within the manure itself. There are many types of manures, each of which are handled differently. Hog manure is different from beef manure, one cow digests the ration slightly different from the others, one group of heifers might be fed a different ration from another group of heifers, some manure is stored for months while some for only a few days. There are also many ways to treat manure. There are untreated lagoons or packs, digesters, solid separators, compost procedures and any combination of the previously listed practices. All of these factors, in addition to others, contribute to the variability that exists even within one tank or spreader full of manure that is hauled to the field. For these reasons, it is difficult to assign one baseline application recommendation to any given type of manure.

A study currently being conducted within the state of Wisconsin is looking at how we can become more efficient with manure applications depending upon the type and treatment of the manure. One hypothesis is that the ratio of total carbon (C) to total nitrogen (N) in manure influences the availability of nitrogen over the growing season.
However, it is unlikely that procedures to measure total C in manure will be widely adopted due to the high per-sample cost of this procedure compared to more routinely used procedures. It has been suggested that a cheaper method for the determination of organic matter by dry ashing may provide suitable information for the estimation of C:N ratio in manure, but as of yet, this theory has not been tested. The objectives of the experiment described in this paper were to 1) evaluate the relationship between total C determined using a Carbon-Nitrogen (CN) analyzer and total C estimated by a dry ashing, and 2) evaluate the relationship between C:N ratio determined by CN analyzer and C:N ratio estimated from using the dry-ash total C and total N determined by the routine Kjeldahl method.

**Materials and Methods**

*Sample Types and Collection*

Two sets of samples were processed during the experiment. The first set included 54 dairy manure samples that were collected for an incubation study being conducted in cooperation with UW- Madison. These samples were collected from five different farms and represent various manure treatment systems including composting (actively turned and bedded pack types), anaerobic digestion (mesophilic and thermophilic systems), and liquid solid separation (both solid and liquid fractions). The second type of samples was a subset of samples received for testing by the University of Wisconsin Soil and Forage Analysis Lab in Marshfield. These samples were analyzed as-received by the Marshfield lab, but were dried and ground prior to analysis with the CN analyzer at UW-Platteville. There were 38 samples that included dairy, chicken, turkey, swine and duck manure.
Each of the 54 incubation and 38 dried samples were tested 3 times for total C and total N using the Elementar vario MAX CN Analyzer, which is maintained in the UW-Platteville soils lab. The CN Analyzer is an automated instrument which completely combusts solid and liquid samples at a temperature of 928 degrees Celsius in the presence of oxygen. During this process, carbon, hydrogen, nitrogen and sulfur present in the sample are oxidized to O₂, H₂O, NOₓ, SO₂ and SO₃. Helium is used as a carrier gas to move the oxidized C and N through the system. The gas travels first through a combustion tube then a post combustion tube, both containing CuO to ensure that all elements are oxidized, then through a drying process to remove water vapor before entering the reduction tube. The reduction tube uses elemental tungsten to absorb sulfur compounds, reduce nitric oxides to N₂, and bind extra oxygen and halogens. N₂ and CO₂ that result need to be measured separately, so the CO₂ is temporarily adsorbed onto heatable columns while the N₂ is flushed through the system. The C and N is determined by a change in thermal conductivity via two thermal conductivity detectors. Standards of known C and N content (L-glutamic acid) are used to calibrate the machine and for quality control check samples. The Instrument determines the percentage of N and C in each sample using the sample weight previously entered into the computer.

The tests used for C and N determination used at the Marshfield lab are the dry ashing procedure and the Kjeldahl N test, respectively. The dry ashing procedure burns the samples at 500 degrees Celsius, burning off the organic matter in the manure. Carbon content is estimated by assuming that the organic matter lost on ignition is 58% by weight C. Using this factor and the loss of weight via combustion, the total organic C can is calculated.
The Kjeldahl N test first involves digesting the samples with concentrated sulfuric acid. After digestion the solution is made alkaline through addition of sodium hydroxide, releasing ammonia gas. The gaseous ammonia is distilled into a dilute HCl solution, converting the ammonia to dissolved NH₄. Ammonium concentration is then determined by titration of the unreacted HCl with standardized NaOH.

**Results**

The dry ashing procedure accurately predicts the total C percentage of the dried samples as seen in Figure 1. The data establishes a trend line with an $R^2$ value of 0.934, indicating a strong correlation between the C content estimated by dry ashing and that determined by the CN analyzer. The relationship between the dry ashing C percentage and the actual amount of C as determined by the CN analyzer is $y = 0.775x + 4.161$, where $y$ represents the C determined by the CN analyzer and $x$ represents the C estimated by the dry ashing procedure.

The incubation samples did not fit as well into a trend line (Figure 2). The $R^2$ value is 0.4858 on the line $y = 0.6304x + 12.309$. The variation in water content of the samples likely added more variability, because C contents did not correlate as well as the solid samples as shown in Figure 3. The solid samples, including separated solids, composts, and pack manures, had an $R^2$ of 0.6857 on the line $0.6587x + 11.193$, where the liquid samples which included raw dairy slurry, separated liquids, and lagoon samples had an $R^2$ of 0.154 along the line $0.4908x + 17.902$. The results of the incubation study samples become more acceptable when analyzing the relationship between the C:N ratio as determined by the dry ashing/Kjeldahl N and the Total C/Total N ratio determined by the CN analyzer (Figure 4). Variation in moisture contents are normalized when the data
is expressed as the C:N ratio, as evidenced by the $R^2$ of 0.9333 determined for the trend line, $y = 0.8683x + 0.0357$, where $y$ is the C:N ratio as determined by the CN analyzer and $x$ is the dry ash C estimation divided by the Kjeldahl N value.

**Discussion**

Based on our results, the proposed method for using the dry ashing procedure to predict total C content is not accurate for the determination of C content in manure samples on an as-received basis, and especially for liquid samples. The variation is too great to confidently use the equations that were derived from our data sets. There is greater accuracy in predicting the C percentage of dried, ground samples but this deviates from the condition of the manure that is actually applied to cropland by producers. However, the procedures were shown to effectively predict the C:N ratio of manure. The ratio is not affected by the water content of the sample, and would therefore allow the cheaper, currently used dry ashing procedure to provide information about the availability of the nitrogen, within the given sample of manure, thus increasing the efficiency of the manure application.

As previously mentioned, the main source of error and reason for the variation in the incubation study is the presence of water. It is difficult to test a truly representative sample of each type of wet manure. For example, the solids in a raw slurry sample will settle out in a matter of seconds if not constantly stirred. You can even observe the solids settle to the bottom of the sample while it is in the pipette between the collection bottle and the crucible used for testing. The variable amount water in each sample makes it difficult to find a reliable trend for predicting total carbon percentage. Since the water makes up a significant portion of the sample weight, the amount of C per unit of weight
(percent C) is difficult to measure. The reason that the C:N ratio data follows a better trend is because the amount of C relative to the amount of N appears to remain fairly constant regardless of the solids content of the sample.

Other potential sources of error could come from the dry ashing C and Kjeldahl N determination. The determination of C using this procedure makes two important assumptions. The first is that only organic matter is burned off during the ignition of the sample. It is the majority of the weight loss, but trace amounts of other substances, particularly volatile compounds that are not necessarily components of organic matter may be lost depending on the composition of the sample, will also be lost. This error would tend to overestimate the amount of C in the sample. The second assumption used by the test is that C accounts for 58% of the organic matter composition. This may be a reliable assumption, but there is little information available regarding the variation in C contents associated with organic matter in manure.

The CN analyzer could also have small amounts of error within its operation. Small gas leaks can occur in many places on the machine. The consumables in the combustion, reduction and drying tubes can also go bad. These problems are likely to be very minor however since the machine monitors itself and alerts you to any functional problems.

Conclusions

Animal manure is an important input for crop production. Efficient nutrient management practices are becoming more important as fertilizer prices continue to rise. By effectively applying manure, a producer can significantly reduce input costs and reduce ecological impacts. The data collected by this experiment has the potential to be
very useful to the future of nutrient management. Further research on the significance of C:N ratio as it relates to nitrogen availability will provide producers and managers with the information needed to efficiently use their manure as a cropping system resource. Being able to use the cheaper, current test methods to accurately predict CN ratio will encourage the use of such information, which could potentially improve the efficiency of using manure as a source of this economically and environmentally important nutrient.

Figure 1. Relationship between %C as determined by dry ashing and %C as determined by CN analyzer - dried, ground samples only

\[ y = 0.775x + 4.161 \]

\[ R^2 = 0.934 \]
Figure 2. Relationship between %C as determined by dry ashing and %C as determined by CN analyzer -N- Fresh manure samples only

\[ y = 0.630x + 12.30 \]
\[ R^2 = 0.485 \]

Figure 3. Relationship between %C as determined by dry ashing and %C as determined by CN analyzer, N incubation study samples only, DM basis

\[ y = 0.4908x + 17.902 \]
\[ R^2 = 0.154 \]

\[ y = 0.6587x + 11.193 \]
\[ R^2 = 0.6857 \]
Figure 4. Relationship between C:N ratios determined by dry ash/TKN and CN analyzer - N incubation study samples