Canadian Journal of Soil Science
Revue canadienne de la science du sol

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Journal:	<i>Canadian Journal of Soil Science</i>
Manuscript ID	CJSS-2016-0103.R2
Manuscript Type:	Article
Date Submitted by the Author:	14-Dec-2016
Complete List of Authors:	Van Andel, Marijke; University of Guelph, School of Environmental Sciences Warland, Jon; University of Guelph, School of Environmental Sciences Zwart, Peter; University of Guelph, School of Environmental Sciences Van Heyst, Bill; University of Guelph, School of Engineering Lauzon, John; University of Guelph, School of Environmental Sciences
Keywords:	ammonia volatilization, Dositube method, semi-open static chambers, calibration

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Development of a simple and affordable method of measuring ammonia volatilization from land applied manures

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Quantifying ammonia (NH₃) flux following fertilizer and manure nitrogen (N) application is crucial to develop sound management practices. Traditional methods used for obtaining these measures are either expensive, inefficient, or inaccurate. The objective of this study is to develop a method using a passive dosimeter and a semi-open static chamber to provide an economical and simple solution to measure NH₃ loss following nitrogen application. Dosimeter tubes were commercially developed to measure ammonia exposure, providing a time-weighted-average. In this study, chicken manure was applied to short grass and the ppm h reading obtained using the dositube ammonia method (DAM) was calibrated against a reference measure of NH₃ loss (kg N ha⁻¹) using a wind tunnel and acid trap method. A calibration was developed (Estimated Total Loss (kg N ha⁻¹) = (0.217Dw) - (0.034D) + 0.71) which requires the dositube (D, ppm hr) to be read every 24 h and placed at a height of 0.15 m in the Dositube chamber, with wind speed (w, m s⁻¹) measured at a height of 0.3 m and averaged over the coinciding time period. This calibration may also be applied where dositubes are read every 48 h; however, 24 h periods are recommended to achieve the greatest accuracy.

Key Words: ammonia volatilization, Dositube Ammonia Method, semi-open static chambers, calibration

INTRODUCTION

Nitrogen (N) loss, through ammonia (NH₃) volatilization can occur from land applied manure and ammonium based N fertilizers causing both inefficiency and uncertainty when

managing N on site (Hargrove et al. 1977; Meisinger et al. 2001; Thompson and Meisinger 2002). Environmental, social, and economical issues arise as a result of NH_3 loss from these sources. Although the process of NH_3 volatilization from manure or fertilizer is well understood (Beauchamp et al. 1982; Harper et al. 1983), quantifying this loss has been difficult and inefficient (Wood et al. 2000; Meisinger et al. 2001).

Ammonia volatilization is a complex process governed by physical, chemical, and environmental factors such as, residue cover, soil pH, form of applied N, wind speed, air temperature, rainfall and incoming solar radiation (Lara Cabezas et al. 1999; Meisinger et al. 2001). Both direct and indirect methods have been used for quantifying NH_3 volatilization. Loss can be estimated indirectly by evaluating the crop response, and by monitoring changes in soil N levels. These methods are imprecise as N losses can also be attributed to leaching, nitrification, or denitrification (Volk 1961); however, with surface fertilizer applications, N losses through these pathways may be minimal in the short term (Hargrove et al. 1977). Similar concerns arise with the use of the ^{15}N balance method, as the amount of NH_3 loss calculated may not account for other N processes. Thus, the direct measure of NH_3 loss is preferred.

There are three main direct outdoor field methods for measuring NH_3 volatilization currently used by researchers: i) micrometeorological (Wilson et al. 1982; Denmead 1983; Harper et al. 1983; Gordon et al. 1988; Warland et al. 2001) ii) Static Enclosure (Volk 1959; Nommik et al. 1973; Kissel et al. 1977; Grant et al. 1996; Lara Cabezas et al. 1999; da Silva Araújo et al. 2009), and iii) dynamic enclosure (Lockyer 1984; Meisinger et al. 2001).

Micrometeorological methods of measuring NH_3 loss such as upwind/downwind methods (Cassel et al. 2005), and localized models such as eddy covariance, typically require costly equipment, technical skills, and large field sites, but are considered to provide the most accuracy, reliability, and allows for continuous monitoring (Denmead 1983; Harper et al. 1983; Warland et al.

2001). The large field sites required for many micrometeorological methods often limit the investigation of NH_3 loss to only one treatment with no replications (Meisinger et al. 2001). Although this method may provide more accurate results, the cost, field size and technical skills required impede the use for many researchers (Lara Cabezas 1999).

The first field chamber method used for measuring NH_3 loss was developed by Volk (1959) to understand the loss of NH_3 following the surface application of urea. Nommik (1973) proposed an improved chamber method consisting of a semi-open static collector with acid soaked sponges placed within the chamber at two heights above the soil surface. Lara Cabezas and Trivelin (1990) evaluated this method using the ^{15}N balance method and found the efficiency (proportion of the NH_3 loss captured without a collector) of the method to be approximately 16.2 % compared to the ^{15}N balance method.

A further modification of a chamber system has been employed to measure in-barn ammonia emission from a manure pack (Acevedo et al. 2009). In that study they made use of the barns air flow pattern to design a chamber that generated a constant air exchange rate and measured NH_3 in the chamber with a photoacoustic gas analyzer. Field sampling is somewhat more complicated due to the complexity of wind direction and speed in the field and often the lack of a power supply for NH_3 analyzers. A variant of dynamic chamber design for measuring NH_3 in the field has been described by Roelcke et al. (2002) and Pacholski et. al. (2006). This method uses “draeger tube method” that require a volume of air to be sucked through the tube at selected measurement times to provide an estimate of NH_3 loss. Pacholski et. al. (2006) found the method resulted in underestimation of loss relative to a micrometeorological method; however, Gericke et. al. (2011) found a good relationship with this method compared to the backwards Lagrangian stochastic dispersion method which is a variant of the micrometeorological method. Although this method is intriguing due to the lack of power requirement and the capacity to measure loss in small

plot research trials, it requires multiple draeger tubes (one for each measurement time) and considerable personnel time to take the measures at the prescribed sampling frequency.

Lara Cabezas et al. (1999) further improved the acid soaked sponge method and stated this method may be used for estimating losses under varying soil, climatic and N fertilizer management conditions. However, Smith et al. (2007) found ammonia losses estimated by the static chamber were underestimated by almost 99 %, when compared to both the wind tunnel and theoretical profile shape methods. Chamber methods allow for an inexpensive, simple, and versatile measure of NH_3 loss. However, the effects of the chamber on environmental conditions including, the process of NH_3 volatilization, are a cause for concern.

Lockyer (1984) developed a dynamic system using small wind tunnels, which allow for small plot measures with little impact on natural conditions. Various studies have since validated and compared this method with micrometeorological methods and found similar results (Smith et al. 2007; Misselbrook et al. 2005; Meisinger et al. 2001), especially when variable speed fans are utilized that can be adjusted to ambient wind speeds (Ryden and Lockyer 1985). The wind tunnel method allows for accurate and relative comparisons between various treatments with replications: however, the cost, analytical analysis, and electrical power requirements limit their use in many field studies.

In summary, a simple and affordable method is required to allow researcher, and potentially farmers and agricultural extension specialist, to measure ammonia loss, particularly when conducting small, multiple plot studies (Lara Cabezas et al 1999). Cost effective methods of quantifying NH_3 loss in the field are limited and the most affordable method used for such research is the acid soaked sponge method by Lara Cabezas et al. (1999). However, the reliability and feasibility of this method is questionable (Smith et al. 2007). An alternative method is needed so that accurate assessments of the impact of NH_3 loss from agriculture practices on the environment

can be made. The proposed dosimeter tube method (Dositube method) may be the solution to measuring this loss.

The Dositube method proposed in this study, consists of a semi-open static chamber (Dositube chamber) placed over a passive dosimeter tube (#3D, Gastec Corporation, 8-8-6 Fukayanaka, Ayase-City, 252-1195, Japan) suspended 0.15 m above the soil surface. Dositubes have previously been studied for their use in poultry facilities and were found to provide a reliable and accurate, time weighted average of NH_3 loss in ppm h (Skewes and Harmon 1995; Wheeler et al. 2000). Research indicates that dositubes may also be useful for measuring NH_3 losses from the field application of manure or fertilizer (Perry 2006). The objective of this research was to develop a simple, affordable, and efficient method for measuring NH_3 volatilization from the field application of manure that provides an immediate measure with no further laboratory analysis.

MATERIALS AND METHODS

Site Description and Experimental Setup

The wind tunnel method developed by Lockyer (1984) was used as the reference measure to calibrate and validate the Dositube method. Other studies assessing the effectiveness of enclosure methods typically calibrate against the ^{15}N balance method (Nommik 1973; Lara Cabezas et al. 1999; da Silva Araújo et al. 2009); however, this method does not account for all losses (Lara Cabazas, and Trivelin, 1990). The wind tunnel method has been shown-to provide accurate accounts of NH_3 loss over different sampling periods and under varying meteorological conditions (Lockyer 1984; Ryden and Lockyer 1985; Meisinger et al. 2001; Smith et al. 2007). The wind tunnel method also allows for the assessment of various application rates with replication that is not easily possible with micrometeorological methods (Lara Cabezas 1999).

Four calibration trials and one validation trial were conducted during the periods of May 18-21, May 24-26, May 27-29, June 7-9, and June 10-12, 2010 at the Turfgrass Research Institute, Guelph, Ontario. Broiler manure was hand surface applied at varying rates of available N to a grass sward to simulate a broadcasted application. Manure was applied at approximately 8:00 am for each trial, with sampling periods occurring at 12, 24, 36, and 48 h after the application. The grass was mown as short as possible (<1 cm) in the areas of manure application. Plant available N in the broiler manure was calculated as the summation of available organic N (30% of the measured organic N in the manure) and all of the ammonium nitrogen (TAN) (OMAFRA, 2010). Two replications of 0, 150, 300 kg available N ha⁻¹ were used for each of calibration trials one (May 24-26) and three (June 7-9), and 0, 37.5, 75 kg available N ha⁻¹ were applied in 2 replications for each of calibration two (May 27-29) and four (June 10-12). For the validation trial (May 18-21), four replications of 200 kg available N ha⁻¹ were applied with two additional wind tunnels and Dositube chambers receiving no manure. Prior to application the manure was thoroughly mixed and three manure samples were taken from each source and sent to University of Guelph's Lab Services (95 Stone Road West, Guelph, Ontario) for analysis (Table 1). The required plot masses of manure were weighed within 1 day prior to the commencement of each trial.

Meteorological Measurements

Meteorological variables were measured during each experiment using a small portable weather station with data collected on a 21X datalogger in 5 min intervals (Campbell Scientific, Incorporated (CSI)). Air temperature and relative humidity (air temperature and relative humidity probe, HC-S3, CSI,) and incoming solar radiation (Campbell Scientific, CM3) were measured at a height of 1 m above the ground. Wind speed was measured using a cup anemometer (03102 Wind Sentry, CSI) at a height of 0.3 m which is just above the height of the top of the Dositube chamber. Wind speed was also measured in the wind tunnels using a hot-wire anemometer (129MSX, Solomat, UK) and recorded on a MPM 4100 Environmental Monitoring System (Solomat, UK).

Soil temperature was measured using temperature probes (TMC6-HA, Onset Computer Corporation), placed diagonally into the soil at a depth of 1-2 cm, and connected to HOBO dataloggers (H08-006-04, Onset Computer Corporation). Soil temperature was measured inside and outside of both the wind tunnel and Dositive chambers. However, previous work by Ryden and Lockyer (1985) indicated that air temperatures were not different inside vs outside of similar wind tunnels to that used in this study, as such air temperature measurements were only taken outside of the chambers and inside of the dositive chamber to determine the impact of the dosimeter chamber.

Ammonia Measurements

Wind Tunnel Method

Six wind tunnel chambers, similar to those described by Lockyer (1984), Thompson and Meisinger (2002), and Rochette et al. (2001), were setup alongside the Dositive method perpendicular to the direction of the prevailing wind. The wind tunnels consisted of a transparent polycarbonate dome that covered a 1 m² area and attached to a compartment housing a fan generating an average wind speed of 1 m s⁻¹ through the tunnel. Acid traps were used to measure the NH₃ volatilization occurring within the wind tunnels and were composed of a cylinder (41 mm O.D., 200 mm height), fitted dispersion tube (250 mm), rubber stopper (#8), and an overflow tube (test tube fitted with a #4 stopper). The acid trap technique can be used to measure the concentration of NH₃ from enclosure methods, like the wind tunnel method, as fast sampling and high sensitivity analysis are not required (Harper 2005). However, great care is needed, such as proper cleaning of glassware between sample timings, with this technique as it is prone to sample contamination. High density polyethylene (HDPE) tubing was used to connect the background (intake) and sample (exhaust) air to the acid traps containing 100 mL of 0.005 M phosphoric acid. Background air was sampled at a height of 0.3 m, 2 m in front of the opening of the tunnel with a 6 m length of HDPE tubing. Sample air was drawn from an L-shaped port, located in front of the fan,

with a 1 m length of HDPE tubing attached to the acid trap. Air was drawn through the acid traps at a rate of approximately 3 L min⁻¹ using a diaphragm vacuum pump. The total volume of air was measured using flow meters (Gallus 2000-G4, QC) and recorded every 12 h when acid traps were replaced. Acid samples were stored in 250 ml Nalgene® bottles and frozen until analysis. Upon completion of all trials, ammonium concentrations (QuickChem® Method 12-107-06-2-A, Lachat Instruments 2003) in the acid traps were measured colourimetrically using Flow Injection Analysis (Lachat Instruments QuikChem® 8000 Series).

The NH₃ flux (F , kg ha⁻¹ h⁻¹) occurring within the tunnels was calculated as follows (eq. 1):

$$F = (f/A) (c_s - c_b) \quad (1)$$

where f is the air flow rate through the tunnel (m³ h⁻¹), A is the manured area covered by the tunnel (0.0001 ha), and c_s and c_b are the NH₃ concentrations of the sample (exhaust) and background air (intake) (kg NH₃-N m³), respectively.

Dositube Method

The Dositube chamber was placed over a dositube (#3D) (Fig. 1) attached horizontally to a stake at a height of 0.15 m. The scale present on the dositubes indicates a measure of the concentration of NH₃ over time (ppm h). However, the ppm h reading does not relate to a mass of N lost per area. Thus, for the purpose of this proposed method, the current scale on the dositube was used as an index value of NH₃ loss within the Dositube chamber.

Manure was applied at the same rates used with the wind tunnels, to circular areas, 1 m in diameter, and the Dositube method was placed in the centre of the manured area. Prior to placing the chamber over the dositube, the sealed end of the tube was removed to allow the measurement of NH₃ loss to begin. The dositubes remained in the chamber for the duration of the experiment and were read every 12 h by removing the chambers momentarily, while simultaneously collecting and replacing the acid traps from the wind tunnel method.

The standard chamber design used with the Dositube method is a round, white pail with a height of 26.5 cm and an inner diameter of 19 cm, amounting to a volume of 15.4 L (Fig. 1) (Van Andel 2010). Eight, 1.27 cm diameter (1/2 inch) holes were drilled into the top of the pail and eight, 1.27 cm diameter holes were drilled 4 cm from the bottom of the pail (Fig. 1). The round design was chosen as it minimizes the possible effect of wind direction, which may influence the air exchange rate of the chambers. This chamber design was also found to give the best balance between measurement variability and dosiube readability (Van Andel, 2010)

A semi-open static chamber is needed when using dosiubes to minimize contamination from neighbouring sources, which is important when conducting small-plot studies (Van Andel 2010). As previously discussed, the chamber affects several environmental factors, which influence the process of NH_3 volatilization. With this method in particular, wind speed is greatly reduced inside the chamber; however, the wind speed will influence the rate of air exchange occurring within the chamber. This had notable effects on the amount of NH_3 measured by the dosiubes. Air and soil temperature were also altered within the Dositube chamber, with air temperature potentially affecting the rate of diffusion of NH_3 through the dosiubes (Gastec) and soil temperature aiding in the volatilization process. Although the chamber conditions may differ from ambient, the calibration should account for the under- or over-estimation of NH_3 loss occurring within the chamber as measured by the dosiubes.

Statistical Analysis

All meteorological and soil temperature data were averaged over the 12 h NH_3 measurement periods. Soil temperature data was log transformed to meet requirements for normality, randomness and homogeneity of residuals. A multiple means comparison test was performed using *Proc MIXED* in SAS (v.9.1., SAS Institute Inc.) to determine differences amongst the temperature and wind speed data collected.

One value was removed from the calibration data set and deemed an outlier, as the dositube reading was low for the rate of N applied. This was attributed to the fact that the dositube was not immediately placed in the Dositube chamber after application, so some of the NH_3 losses were not accounted for. Two values were removed from the validation data set as these two values were almost three times greater than the other two replicates in that sampling period. Even with the mixing done it is possible that the manure from these replicates may have had a greater percentage of $\text{NH}_4\text{-N}$ and thus were considered outliers. These omissions removed 3 out of a total of 96 of the 12 hour measures of N loss from the data set.

Stepwise regression analyses were completed using the individual plot data (93 data points in total as indicated above) using *proc GLM* to determine the parameters that significantly affected the measurements made with the Dositube method using Type III sums of squares. The NH_3 volatilization data collected from the wind tunnel and Dositube ammonia methods were skewed, due to little to no changes in dositube readings during the night time period (8:00 pm to 8:00 am), but a log transformation did not improve the normality of the data or the fit of the calibration model, so the untransformed data was accepted. When removing the night time data from the calibration data set, the daytime data met the assumptions necessary for such an analysis, with the normality of residuals significant at $P = 0.01$, although terms within the model, such as wind speed and temperature, were not completely independent of each other. Significant parameters were determined with this data set, and these parameters were then considered in the model with all of the data included. All variables and combinations were included in the model and then with each successive regression run, the least significant parameter was removed. The analysis was repeated until only significant terms remained.

Several calibration models were developed from the stepwise regression analysis, ranging from a simple model that incorporated only the total index value accumulated using the dositubes,

to a calibration that incorporated both temperature and wind speed. These analyses were conducted to see if a simpler model was just as valid for use with the Dositube method. Calibration models were also assessed with averaging and sampling periods of 24 h to account for night time conditions. Data were averaged from 0-24, 12-36 and 24-48 h after the application of manure for this analysis.

RESULTS AND DISCUSSION

Meteorological Conditions

Similar meteorological conditions were found for calibration trials 1 and 2 as well as for trials 3 and 4 (Table 2). Air temperature and wind speed varied from 5.0 to 29.5°C and 0 to 3.5 m s⁻¹, respectively, during the duration of the various trials. Rainfall was negligible for each trial (<1 mm total for all trials).

Soil and air temperature data were combined for all five trials. Generally, soil temperature without a Dositube chamber was higher than soil covered with a chamber, especially during daytime conditions. The Dositube chambers provided a shading effect, mitigating the effects of solar radiation on the area covered. Soil temperature without a chamber was warmer than the Dositube chamber by 3.0°C, with only a 2.3°C difference between the wind tunnel and ambient soil temperature during daytime conditions (Table 3). Ryden and Lockyer (1985) also observed a temperature difference between the inside and outside of the wind tunnel to be 1.9°C and stated that only large differences in temperature may be deemed as notably different due to the difficulty in placing temperature probes in comparable positions in a grass sward. During the night time period a significant difference ($P \leq 0.05$) was observed between soil temperatures with and without a Dositube chamber, with an average difference of 1.0 °C, with no difference between the inside and outside of the wind tunnel chambers (Table 3).

The Dositube chamber air was found to be warmer than ambient during the day by as much as 6.6 °C, but was cooler at night. Although air temperature was not measured within the wind tunnels, several studies have measured this parameter and found little differences between ambient and wind tunnel air temperatures (Lockyer 1984; Ryden and Lockyer 1985; Smith et al. 2007).

Although air and soil temperature differences still existed between the conditions within the Dositube chamber and ambient, and thus may influence NH₃ loss, these parameters are only important to assess if there are significant effects on the calibration of the method itself. The data from this trial and previous work by the corresponding author, indicates that the dosiubes can account for variables that affect the driving force, or rate of NH₃ loss within the chamber such as, type, timing of application, rate and placement of manure and fertilizer (Perry 2006, Curtis 2013, Crittenden 2005, Turnbull 2010) and presumably temperature and pH. However, factors that influence the air exchange rate in the chamber, such as chamber design and wind speed, are likely to impact the concentration of NH₃ in the chamber and the dositube measurement.

Overall, the wind tunnel conditions did not vary greatly from ambient, indicating losses in the wind tunnel may be similar to that occurring without the presence of a plexiglass chamber. The wind tunnels were set up perpendicular to the prevailing winds and achieved an average wind speed of 1.0 m s⁻¹ (±0.05 m s⁻¹). The measured ambient wind speed was significantly lower (table 2) than the wind tunnel setting for trials 1 and 2; however, the ambient wind speed for trials 3 and 4 was not significantly different from 1 m s⁻¹. Although this may cause some concern for the validity in using the wind tunnel as a reference method, wind speed was not the dominant factor affecting NH₃ loss. During the 12 h night time flux measurements, wind tunnel measured NH₃ loss was less than 0.1 kg N ha⁻¹ h⁻¹ in most cases (Table 4). This indicates that temperature/solar radiation may have a more notable affect on facilitating NH₃ loss (Brunke et al. 1988) even when wind speed is constant inside the tunnels.

Method Assessment

Ammonia flux, as measured in the wind tunnels, varied from 0.02 to 2.96 kg N ha⁻¹ h⁻¹ for the various treatments during the 48 h duration of the trials, with the greatest flux occurring during the first 12 h for all treatments (Table 4). Similar to the findings of Brunke et al. (1988), the NH₃ flux on the second day (or 36 h after application) was approximately 70% less than the losses occurring in the first 12 h after application (Table 4). The average total loss of NH₃ from an application of 150 kg plant available N ha⁻¹ was found to be approximately 23 kg N ha⁻¹ or 36 % of TAN applied in a 48 h period using the wind tunnel method. Sharpe et al. (2004) found similar results with losses ranging from 36 to 64% of TAN within 48 h after the application of poultry litter. Ammonia flux followed a diurnal pattern, with losses decreasing substantially during the night time periods (12 to 24 and 36 to 48 h after application) due to decreasing temperature (Smith et al. 2007, Rochette et al. 2001, Beauchamp et al. 1982), but more likely due to the effects resulting from solar radiation (Harper et al. 1983) (Table 4).

Several parameters including, wind speed, air temperature, relative humidity solar radiation, and soil temperature were assessed for the influence on the dositube measure for determining observed NH₃ loss as measured by the wind tunnel method:

$$\text{Wind tunnel method (kg ha}^{-1}\text{) loss} = D \cdot \text{Wind} + D \cdot \text{AirTemp} + D \cdot \text{RH} + D \cdot \text{Solar} + D \cdot \text{Soiltemp}$$

where:

$$D = \text{Dositube measurement (ppm h}^{-1}\text{)}$$

$$\text{Wind} = \text{windspeed (m s}^{-1}\text{)}$$

$$\text{AirTemp} = \text{air temperature (}^{\circ}\text{C)}$$

$$\text{RH} = \text{relative humidity (\%)}$$

$$\text{Solar} = \text{Solar Radiation (W m}^{-2}\text{)}$$

The interaction between the dositube reading and wind speed, air temperature, relative humidity, and chamber soil temperature were found to be significant ($P \leq 0.05$) in estimating observed losses (wind tunnel measure). However, all parameters were found to be dependent on one another, and therefore, challenge the assumptions necessary for such an analysis (Bowley 2008). Thus, solar radiation, relative humidity, and soil temperature (which were all correlated and directly related to air temperature) were removed from the model. Although a relationship also exists between air temperature and wind speed, these variables were thought to affect the dositube measure in different ways due to the nature of the chamber design and the dositube itself, as previously discussed. The interactions of these two parameters were assessed in developing the calibrations for the Dositube method using a multiple linear stepwise regression analysis in SAS.

The final parameters remaining in the model were significant at $P < 0.0001$ and included both air temperature, wind speed and air temperature interactions with the dositube measure (D):

*Wind tunnel method (kg ha⁻¹) loss = (D) + D*AirTemp + D*Wind*AirTemp where:*

D = Dositube measurement (ppm h⁻¹)

Wind = windspeed (m s⁻¹)

Air Temp = air temperature (°C)

Several calibration models were developed which used only wind speed or temperature effects to determine the simplest equation that could be used to model loss. The results indicated that eliminating temperature from the model did not change the fit of the model appreciably ($R^2 = 0.972$ to 0.966), thus, the temperature variable was removed from the model. When wind was removed and only temperature remained the R^2 decreased to 0.919 and systematic bias was observed with respect to wind speed. The model incorporating only air temperature and the tube

reading appeared to overestimate losses at wind speeds greater than 1 m s^{-1} and underestimate losses when wind speeds were less than 1 m s^{-1} .

Thus, the calibration resulting from this analysis includes: ambient wind speed measured at 0.3 m above the soil surface (w , m s^{-1}), and the dositube measurement (D , ppm h) based on 12 h sampling periods (eq. 2):

$$\text{Estimated Total Loss (kg N ha}^{-1}\text{)} = (0.118Dw) - (0.028D) + 0.74 \quad (2)$$

A strong correlation existed between the observed and estimated losses ($R^2 = 0.966$) with a slope of 0.95. When applying this calibration to the validation dataset, a slope of 0.85 and a R^2 value of 0.807 were found. The model slightly overestimated actual losses by an average of 0.49 (0.875) kg N ha^{-1} . The standard deviation of the deviations between observed and estimated was approximately 1.0 kg N ha^{-1} .

No systematic bias was observed when wind speed, air temperature, or observed losses were plotted against the deviations from this model, when applied to either the calibration and validation datasets. This indicates that wind speed was the dominant environmental parameter effecting the dositube measurement as it relates to actual loss. This may be due to the effect wind speed has on the rate of air exchange in the Dositube chamber. As wind speed increases, the level of NH_3 measured by the dositube may be lower in the chamber due to increase air mixing. Shigaki and Dell 2015 also concluded that wind speed was a major factor impacting semi-open ammonia collection chamber readings.

24 hour sampling calibration

A 12 h sampling period is not always realistic for all researchers and often measurements may only take place every few days. Thus, a similar modeling exercise was performed on a 24 h dataset as the 12 h dataset previously described. A 24 h calibration was obtained from this analysis,

which included: ambient wind speed measured at 0.3 m above the soil (w , m s^{-1}) and the dositube measurement (D ppm h) based on 24 h sampling periods (eq. 3):

$$\text{Estimated Total Loss (kg N ha}^{-1}\text{)} = (0.217Dw) - (0.034D) + 0.71 \quad (3)$$

This 24 h calibration model provided a strong relationship between observed and estimated losses ($R^2 = 0.977$) with a slope of 0.97 (Fig. 2). The model appeared to overestimate losses when applied to the validation dataset by approximately 10 % (Fig. 3), with a mean value of 0.71 (0.985) kg N ha^{-1} .

No obvious systematic bias was observed for the calibration or validation datasets when evaluating the computed loss with the observed N loss, wind speed or temperature, demonstrating the effectiveness of the model (Fig. 4 and Fig. 5).

This calibration based on 24 h periods was applied to the dositube measures taken 48 h after application, with wind speed averaged over the 48 h period. The calibration and validation datasets were combined for this analysis. A strong correlation was found between the observed and estimated losses with a slope of 0.93 and a R^2 value of 0.986 (Fig. 6). The intercept of the linear regression was not significant ($P = 0.5323$), indicating the dositubes may account for low levels of NH_3 loss when longer sampling periods are used (Fig. 6).

Deviations of the computed values from the observed values varied from -5.38 to 2.06 kg N ha^{-1} , with the model slightly underestimating loss by an average of -0.94 (1.996) kg N ha^{-1} over a 48 h period (Fig. 7). No systematic bias was observed with the deviations of the observed N loss, wind speed, or temperature, indicating the effectiveness of the 24 h calibration applied to the 48 h dataset (Fig. 7).

CONCLUSION

Based on this calibration and validation study, the overall accuracy of the Dositube method appears to vary with a standard deviations of 1 to 2 kg N ha⁻¹ depending on the length of the measurement period. The accuracy of the Dositube method is well within the variation observed by the acid soaked sponge method and considering the cost and complexity of other methods used to measure total NH₃ loss, the Dositube method appears to be a viable alternative. This method allows for a simple, cost-effective and immediate measure of total NH₃ loss over a given time period.

The calibration did not appear to be affected by the rate of volatilization as influenced by factors such as temperature, relative humidity, etc provided windspeed was included in the model. This would indicate that the tubes are capable of measuring a wide variation in NH₃ loss; thus, this method may also be suitable for measuring NH₃ loss from other N sources. However, wind speed was found to alter the dosiube measurements likely due to the impact wind has on the rate of air exchange in the chamber, which may reduce the residence time of NH₃ in the chamber, or increase the dilution of the NH₃ with outside air.

It appears that the accuracy of the Dositube method decreases when averaging time increases, although the sensitivity may increase with longer measurement periods than used in this study. Caution should also be taken when applying these calibrations to conditions/parameters outside of this study such as, when wind speeds are greater than 3 m s⁻¹ or when losses are measured from bare soil or within a crop canopy. Work by the corresponding author since the development of this method (Curtis, 2013) and a variant of this method from before development (Crittenden, 2005, Perry, 2006, Turnbull 2010) under a range of application methods, amendment types, and timings of application have provided relative ammonia loss data. These data indicate that relative ammonia loss using the dosiube ammonia method is capable of differentiating among these treatment effects factors impacting the ammonia emission rate. However, it is less capable of dealing with factors not related to treatments such as wind speed that may impact air exchange rates in the chamber. Therefore, it is suggested that further calibration efforts on these factors. .

This calibration experiment was conducted over a grassy surface, although cut very short (<1cm) may alter wind speeds near the surface, compared to completely bare soil. Similarly, a crop canopy may alter the surrounding air ammonia concentrations relative to a bare soil environment which may impact the ammonia concentration of the air exchanging with the chamber. Another area for study not considered in this study could determine if chambers should be moved following a rainfall. This would indicate whether the drier soil under the chambers affect ammonia loss measurements

The authors encourage more research to further validate the calibration presented. The Dositube ammonia method should be compared against a reference method such as the micrometeorological, mass balance or wind tunnel methods that do not affect the volatilization process. The effectiveness of this method should also be compared under a variety of physical and chemical conditions.

ACKNOWLEDGEMENTS

This project was funded by the OMAFRA - U. of G. Partnership, Poultry Industry Council, Canadian Poultry Research Council and NSERC CRD. Special thanks are extended to Peter von Bertoldi for his advice and assistance.

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Table 1. Analysis of fresh weight broiler manure from two different broiler facilities near Guelph, ON used for the calibration (Easteop) and validation (Laird Rd.) experiments in 2010

Location	Characteristics	Average Value
Easteop Farms	Total N	3.11%
	TAN*	5797 mg kg ⁻¹
	Dry matter Content	67.9%
Laird Rd. Facility	Total N	3.25%
	TAN	6643 mg kg ⁻¹
	Dry matter	65.6%

*total ammonium nitrogen

Table 2. Average meteorological values (SD) for the calibration (Cal) and validation trials (48 h averages) conducted at the Turfgrass Research Institute, University of Guelph, Guelph, ON, 2010

Trial no.	Date (2010)	Ambient Air Temp. at 1 m (°C)	Wind Speed at 0.3 m (m/s)
Cal - 1	May 24-26	21.5 (4.99)	0.50 (0.75)
Cal - 2	May 27-29	21.1 (4.76)	0.54 (0.89)
Cal - 3	June 7-9	13.4 (3.95)	1.03 (0.58)
Cal - 4	June 10-12	16.6 (4.06)	0.89 (0.54)
Validation	May 18-21	15.5 (6.43)	0.87 (0.96)

Table 3. Average soil and air temperature measured with and without Dositube chambers as well as soil temperature measured inside the wind tunnel chambers. Mean (SD) values presented are an average of all trials when the respective measures took place at the Turf Grass Research Institute, University of Guelph, Guelph, ON, 2010

Chamber	Daytime (8 am to 8 pm)		Night time (8 pm to 8 am)	
	Soil Temperature ^a mean (SD) (°C)			
None	22.3 (4.64)	<i>a</i>	15.1 (2.93)	<i>ab</i>
Wind Tunnel	20.0 (3.19)	<i>b</i>	15.6 (2.48)	<i>a</i>
Dositube Chamber	19.3 (4.12)	<i>c</i>	14.7 (2.65)	<i>b</i>
Chamber	Daytime (8 am to 8 pm)		Night time (8 pm to 8 am)	
	Air Temperature ^a mean (SD) (°C)			
None	20.6 (1.17)	<i>a</i>	10.0 (1.71)	<i>a</i>
Dositube Chamber	24.8 (2.44)	<i>b</i>	9.1 (0.22)	<i>b</i>

^a*a-c* means followed by the same letter are not significantly different at P=0.05 using a multiple means comparison test. Means and standard deviations calculated arithmetically.

Table 4. Average NH₃ flux (SD) measured by the wind tunnel method from each application rate (kg avail N ha⁻¹) for each calibration (Cal) and validation trials at 12, 24, 36 and 48 h after application of broiler manure at the Turf Grass Research Station, University of Guelph, Guelph, ON, 2010

	Cal-1		Cal-2		Cal-3		Cal-4		Validation	
	----- Application Rates (kg ha ⁻¹) -----									
Time (h)	150	300	37.5	75	150	300	37.5	75	200	
	----- Flux (kg N ha ⁻¹ h ⁻¹) (SD) -----									
12	1.32 (0.011)	2.06 (0.502)	0.37 (0.092)	0.67 (0.010)	1.38 (0.268)	2.95 (0.338)	0.45 (0.031)	0.72 (0.079)	0.54 (0.078)	
24	0.11 (0.016)	0.14 (0.029)	0.03 (0.006)	0.07 (0.073)	0.10 (0.020)	0.21 (0.006)	0.06 (0.020)	0.05 (0.002)	0.06 (0.059)	
36	0.45 (0.039)	0.72 (0.047)	0.12 (0.021)	0.23 (0.021)	0.38 (0.014)	0.72 (0.081)	0.19 (0.035)	0.27 (0.005)	0.21 (0.101)	
48	0.09 (0.053)	0.07 (0.026)	0.02 (0.005)	0.02 (0.015)	0.05 (0.010)	0.10 (0.025)	0.06 (0.003)	0.05 (0.014)	0.05 (0.008)

Fig. 1. Chamber design used for the Dosimeter method showing placement of holes at top (a) of pail and around the base of the pail (b) to minimize contamination of neighbouring NH₃ sources on the dosimeter tube (c) reading, but still allow for some air exchange to occur.

Fig. 2. 24 h calibration model applied to calibration dataset.

Fig. 3. 24 h calibration model applied to validation dataset.

Fig. 4. Deviations from Observed for 24 h calibration applied to 24 h calibration dataset.

Fig. 5 Deviations from observed for 24 h calibration applied to 24 h validation dataset.

Fig. 6. 24 h calibration model applied to 48 h data set (validation and calibration data combined).

Fig. 7. Deviations from observed for 24 h calibration applied to 48 h calibration and validation dataset.