Measurement of nitrous oxide concentrations from Wisconsin dairy barns

Neslihan Akdeniz
Dept. of Bioproducts and Biosystems Engineering, University of Minnesota, St. Paul, MN 55108

Larry D. Jacobson
Dept. of Bioproducts and Biosystems Engineering, University of Minnesota, St. Paul, MN 55108

Brian P. Hetchler
Dept. of Bioproducts and Biosystems Engineering, University of Minnesota, St. Paul, MN 55108

Rodney T. Venterea
Soil and Water Research Management Unit, USDA-ARS, St. Paul, MN 55108

Kurt A. Spokas
Soil and Water Research Management Unit, USDA-ARS, St. Paul, MN 55108

Written for presentation at the 2009 ASABE Annual International Meeting
Sponsored by ASABE
Grand Sierra Resort and Casino
Reno, Nevada
June 21 – June 24, 2009

Abstract. Nitrous oxide (N\textsubscript{2}O) is one of the important greenhouse gases. N\textsubscript{2}O emissions from anthropogenic sources are approximately 7-8 million tones N/yr worldwide and 70% of these emissions are caused by crop and animal production. In this study, direct N\textsubscript{2}O production from dairy cattle (enteric fermentation) and feces/urine temporarily stored in two freestall dairy barns were measured with 1) photoacoustic infra-red gas analyzer I (analyzer I, Innova 1412), 2) infra-red gas analyzer II (analyzer II: Teledyne API 320E), 3) GC-ECD (gas chromatography-electron capture detector), and 4) GC-MS (gas chromatography-mass spectroscopy). N\textsubscript{2}O concentrations in the exhaust air from the two barns ranged from 310 ppb to 371 ppb. No significant difference was found between GC-ECD and GC-MS N\textsubscript{2}O results. Analyzer II's response was not sensitive enough for the near ambient N\textsubscript{2}O concentrations found from the two dairy barns. Significant differences were found between GC-ECD and analyzer I N\textsubscript{2}O measurements. These differences may be caused due to interferences between N\textsubscript{2}O and CO\textsubscript{2} and water vapor.

Keywords. Dairy barn, GC-ECD, GC-MS, infra-red gas analyzer, nitrous oxide.
Introduction

Nitrous oxide (N₂O) is one of the important greenhouse gases. It has 297 times more global warming potential than CO₂ and a long (up to 150 years) atmospheric lifetime (IPCC, 2001). It also plays an important role in depletion of the ozone layer (Bolin et al., 1981). The atmospheric concentration of N₂O has increased 16 % in the last 250 years and continues to increase (IPCC 2001). Presently the concentration of N₂O in the atmosphere is 310 ppb and it is expected to reach 415 ppb by the end of the next century (Kawashima et al., 1996). N₂O emissions from anthropogenic sources are approximately 7-8 million tonnes N/yr worldwide and 70% of these emissions are caused by crop and animal production (van Aardenne et al., 2001).

There are direct and indirect sources of agricultural N₂O production (Mosier et al., 1998). In this study, direct N₂O production from dairy cattle (enteric fermentation) and feces/urine temporarily stored in barns were measured. Different N₂O measurement methods were compared since the majority of direct N₂O measurements are of questionable quality. Many N₂O detection studies rely on photoacoustic spectroscopy analyzers (Drescher and Brown, 2006). These analyzers may require removing CO₂ and water vapor from samples since they can interfere with N₂O sensing. In this study, N₂O concentrations of the dairy barns were measured using 1) photoacoustic infra-red gas analyzer I (analyzer I, Innova 1412), 2) infra-red gas analyzer II (analyzer II: Teledyne API 320E¹), 3) GC-ECD (gas chromatography-electron capture detector), 4) GC-MS (gas chromatography-mass spectroscopy). The purpose of the study was to use GC-ECD and GC-MS as standard methods and check reliability of the continuous infra-red gas analyzers to measure N₂O concentrations from the two dairy barns.

Methodology

Sampling site

The N₂O samples were collected from two mechanically ventilated, freestall dairy barns (barn 1 and barn 2) located near Baldwin, Wisconsin. There were 250 dairy cattle in barn 1 and 350 dairy cattle in barn 2. Samples were drawn from a representative exhaust air stream (suction side of continuous running exhaust fan) of each barn using isolated Teflon tubing and compared with ambient air entering the barns.

Infra-red gas analyzers

Infra-red gas analyzers measured real time N₂O concentrations. These instruments were set to collect data every minute and the average of 60-min sampling was reported. Analyzer II responded to calibration gas at one ppm concentration but did not respond to concentrations below one ppm.

Analyzer I was calibrated on weekly basis. Zero air (Teledyne zero air module 701), and three concentrations of N₂O (2, 4, 8 ppm) prepared by a gas dilution system (Environics 4040) were used to prepare calibration curve for the Innova 1412. To prevent cross compensation between gases, this instrument was also pre-calibrated by the supplier considering average CO₂ and water vapor emissions from dairy barns.

¹ A more sensitive model (320EU) from this manufacturer (Teledyne API) is available. As a result of our findings in this study, the existing 320E is being upgraded to the 320EU quality for a subsequent study.
**GC-ECD and GC-MS**

Nitrous oxide measurements were made in USDA-ARS Soil and Water Research Management Unit, on the St. Paul campus of the University of Minnesota. Air samples were drawn from 10 L Tedlar bags (n=2 ambient air, n=3 barn 1, n=3 barn 2) collected over 60 minute time span for each source. At the end of the 60 min, 10 mL samples were transferred from Tedlar bags into small glass vials using a syringe. Before sample collection, glass vials sealed with butyl rubber septa were flushed with He (10 psi) for one min.

Glass vial contents were analyzed by GC-ECD and GC-MS. The GC (Agilent 5890)-ECD (HP/Agilent) system was equipped with a headspace auto-sampler (Teledyne Tekmar 7000/7050). The system used a Porapak Q 80/100 mesh packed column (3.17 mm×1.83 m) and He carrier gas (20 mL/min). The GC (Perkin Elmer Calrus 600)-MS (Perkin Elmer 600T) was also equipped with a headspace auto-sampler (Agilent 7694). RT-QSPLOT (0.32 mm×30 m) column with He carrier gas (2 mL/min) was used to detect N$_2$O peak. The systems were calibrated using analytical grade standards (Venterea et al., 2005).

**Statistical analysis**

Data were analyzed using the statistical package JMP v. 6.0.2 (SAS Institute, Inc., Cary, NC). Data were subjected to a one-way analysis of variance (ANOVA). Treatment means were compared using TUKEY’s honestly significant differences (HSD) test at the 95% confidence level.

**Results and discussion**

Average N$_2$O concentrations for ambient air, barn 1, and barn 2 are shown in Figures 1, 2, and 3. At the beginning of the study (12-02-08 and 12-16-08), GC-ECD and GC-MS results were compared and no significant difference was found between results of ECD and MS detectors (Figure 1). After the first one month, samples were collected for only GC-ECD analysis and GC-ECD results were compared with infra-red gas analyzers’ results (Figure 2 and 3).

![Figure 1. Comparison of average N$_2$O concentrations measured by GC-ECD and GC-MS (n=2 ambient air, n=3 barn 1, n=3 barn 2). Means (within a sampling location) that are not associated with the same letter are significantly different (α=0.05).]
Figure 2. Comparison of average N₂O concentrations measured by GC-ECD, analyzer I, analyzer II. Means (within a sampling location) that are not associated with the same letter are significantly different ($\alpha=0.05$).
The results of analyzer II were found to be significantly different than the GC-ECD results (Figure 2). Standard deviation of the data was high and relative standard deviation ranged from 3.96 to 157%. This instrument was not sensitive enough for the near ambient N₂O measurements found in these dairy barns. The lower detection limit of the instrument was reported as 40 ppb, but the instrument did not respond well to ambient level concentrations (310 ppb).

In Figures 2 and 3, the results of GC-ECD and analyzer I are compared for eight different sampling dates. Although N₂O concentrations measured by GC-ECD and analyzer I results were close, statistically significant differences were observed for most of the sampling dates (e.g., 3-31-09). These differences may be caused due to 3 reasons:

i. Different sampling methods were used to collect GC-ECD and analyzer I samples. To minimize the effect of sampling, samples for GC-ECD and analyzer I were collected simultaneously. For GC-ECD analysis, air samples were collected inside Tedlar bags for 60 min and at the end of the 60 min, 10 mL samples were drawn from Tedlar bags. Analyzer I measured real time N₂O concentrations for 60 min (simultaneously with Tedlar bag sampling).

ii. Calibration and calculation mistakes. Calibration curves for analyzer I were prepared on a weekly basis. For GC-ECD measurements analytical grade standards were run at the beginning and end of the each sample batch.
iii. Cross compensation of CO₂ and water vapor with N₂O. Although analyzer I was calibrated considering average CO₂ and water vapor emissions from dairy barns, high CO₂ and water vapor concentrations might influence N₂O readings. The CO₂ concentrations of the barns ranged from 500-800 ppm (12-02-08, 2-17-09, 3-17-09, 3-31-09, 4-14-09) to 1100-1700 ppm (12-16-08, 1-13-09, 1-27-09). Dew point temperature of the samples drawn from barns ranged from (-9)-(-0.1) ºC (12-02-08, 12-16-08, 01-13-09, 01-27-09, 02-17-09, 04-14-09) to 2-8 ºC (03-17-09, 03-31-09). These wide ranges of CO₂ and water vapor probably affected N₂O readings. Analyzer I can overestimate N₂O emissions from dairy barns and this should be taken into account during measurements.

Conclusions

Nitrous oxide concentrations in the exhaust air from dairy barns were measured every other week from 12/02/08 to 4/14/09. Four different instruments (GC-ECD, GC-MS, infra-red gas analyzer I, and infra-red gas analyzer II) were used to make N₂O measurements. N₂O concentrations of the barns ranged from 310 ppb to 371 ppb.

No significant difference was found between GC-ECD and GC-MS N₂O concentrations. Analyzer II was not sensitive enough for the near ambient N₂O concentrations found from the two dairy barns. Significant differences were found between GC-ECD and analyzer I N₂O concentrations. Although the instrument was calibrated at the beginning of the study and weekly basis, N₂O measurements might be affected by the wide range of CO₂ and moisture levels (dewpoints) from dairy farms.

Acknowledgements

The authors would like to thank the University of Minnesota’s Agricultural Experimental Station’s Rapid Response Fund for supporting this research.

References