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Field comparison of static and flow-through chamber techniques for measurement of soil NO emission

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Abstract. A field comparison of flow-through and static chamber techniques for measuring soil emissions of NO was performed on fertilized soil at a commercial cotton (*Gossypium hirsutum L.*) farm near Muscle Shoals, Alabama, during July 1992. The purpose of the study was to compare soil NO_x emissions data taken using two different techniques at a common field site. Emission rates with collocated chambers using the two techniques were compared, and spatial means were also compared for 17 National Oceanic and Atmospheric Administration (NOAA) plots and 10 Tennessee Valley Authority (TVA) plots. Emission rates of NO at the site covered a broad spectrum, ranging from less than 1 to greater than 100 ng N m^{-2} s^{-1}. Data from collocated TVA static and NOAA flow-through chambers showed a correlation coefficient of 0.98 with a linear regression slope of 0.97. A *t* test indicated that the mean difference was not statistically different than zero. The plot mean emission rates were 17.7 and 18.0 ng N m^{-2} s^{-1} for the TVA and NOAA chambers, respectively, for an 8-day comparison period. These findings indicate that data sets collected with these methods are comparable and may be combined without concern for differences in technique. These results also reveal that the techniques used by each group in attempting to characterize overall site mean emissions are remarkably similar, despite differences in chamber size, plot location, extent of areal coverage, and random error associated with the measurements. This finding is significant in that it means that field data used to characterize emissions estimates by both protocols can be pooled to better estimate regional soil NO emission inventories.

Introduction

The main source of NO_x ($NO + NO_2$) in the atmosphere is from human activity, chiefly combustion of fossil fuels (40%) and biomass burning (25%) [*Logan*, 1983]. However, there also exists a biogenic component that is related to the emission of NO_x from soils. An understanding of the magnitude and extent of soil NO_x emissions is essential in attempting to better understand the factors contributing to tropospheric ozone (O_3) formation, since O_3 production has been shown to be related to atmospheric NO_x levels [*Liu et al.*, 1987]. High O_3 levels are known to have a detrimental effect on crop production and human health [*Graham et al.*, 1990; *Shriner et al.*, 1990]. Thus characterization of this soil source of NO_x is extremely important.

Recent measurements of soil NO_x emissions have indicated that in some instances comparable emissions exist between anthropogenic sources in urban areas and soil sources in rural agricultural areas [*Valente and Thornton*, 1993; *Williams et al.*, 1992a], so clearly, the emission of NO_x from soils is a nonnegligible source. However, the assessment of this source is highly uncertain owing to the limited measurements that have been made, large temporal and spatial variability of emission rates, and possible differences in published data owing to differences in measurement methodologies.

Several techniques have been employed to determine soil emissions of NO_x. Most of these methods are chamber or enclosure techniques, but distinctive differences among them are apparent. One important difference is the choice of static or dynamic treatment of the interior air of the chamber. The static chamber method utilizes the buildup in concentration within the chamber over a specified period of time to determine the soil NO_x emissions. The dynamic, or flow-through, chamber method utilizes an airflow to continually flush the chamber interior, and the flux is calculated from mass balance considerations once the NO level reaches a steady state. Both methodologies have advantages and disadvantages, but to date there has been no field comparison of these two techniques to assess comparability of the data obtained by them. However, a previous study [*Williams and Davidson*, 1993] reported good agreement for a comparison between two dynamic chamber methods. The study reported here is a comparison of soil NO_x emissions measurements made by static and dynamic chamber methods in an agricultural field site. The results of this study are intended to address the issue of comparability of soil NO_x emissions data by these different techniques at a common field site.

Experimental Site

The comparison was performed at a commercial cotton (*Gossypium hirsutum L.*) farm near Muscle Shoals, Alabama, during July 1992. The soil type at this site is an Etowah silt-loam (Typic Paleudult). A no-tillage system was used in which cotton was planted in alternating row widths of 1.2 and 0.6 m into a winter wheat cover crop (*Triticum aestium L.*). A mid-March application of fertilizer containing 11 kg N ha^{-1} was broadcast to promote late season wheat growth prior to killing

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the crop by the application of glyphosphate before planting cotton in mid-April. Anhydrous ammonia was banded at the rate of 112 kg N ha^{-1} next to the cotton rows in early May. At the time of the intercomparison, cotton plants were present on the field and had reached a height of about 60 cm. This site was selected for the intercomparison because it was expected to show a large range of NO flux values based on the fertilizer application and the time of year. Because fertilizer had been applied in a banded fashion, it was hoped that emission rates would show significant spatial variability, allowing for a broad range of emission rates to be represented in the intercomparison. The summer season was selected for the study because it was anticipated that hot temperatures interspersed with thunderstorm activity would lead to alternating dry and wet soils, providing significant temporal variability in emissions as well. Plots were chosen randomly both between and within cotton rows. A schematic representation of the chamber locations within the field is shown in Figure 1. Throughout this paper the Tennessee Valley Authority (TVA) and National Oceanic and Atmospheric Administration (NOAA) plots are referred to with the numbers and letters shown in Figure 1. Soil temperature (thermocouple), air temperature (thermistor), precipitation (tipping bucket rain gage), and soil moisture (gypsum block) were monitored continuously to provide information potentially helpful in interpreting the results. Upon completion of the experiment, soil samples were taken at each sampling location to determine soil chemical properties.

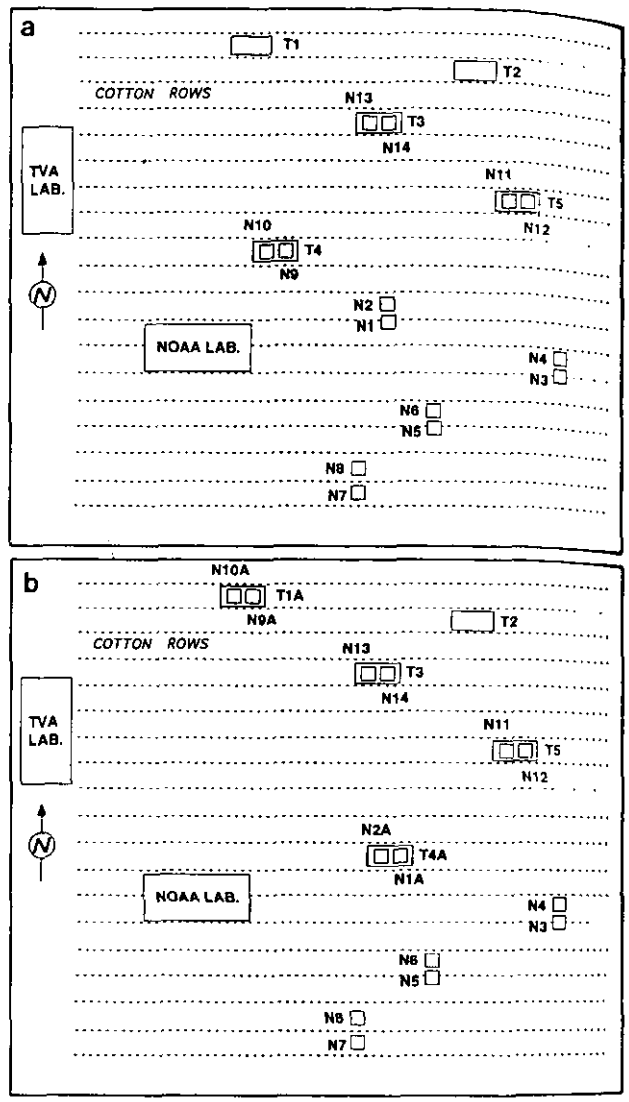

Figure 1. Schematic diagram of the site configuration showing (a) the location of TVA plots (locations with prefix T) and NOAA plots (locations with prefix N) prior to 1500 CDT on July 10, 1992 and (b) the plot locations after 1500 CDT on July 10, 1992. In Figure 1b the suffix A indicates the new plot locations except for T1A and N2A. These two locations were the same throughout the study, but new designations were assigned to indicate that the data have been segregated in time.

Measurement Techniques

The NOAA flow-through technique [*Williams et al.*, 1988] uses a transparent chamber with perfluoralkoxy (PFA) Teflon film walls. The chamber (30 cm × 30 cm × 30 cm) is placed on a stainless steel frame driven into the soil to a 10 cm depth. In sunny weather a white cloth is placed over the chamber to reduce heating of the soil when the chamber is in use. Dry zero air (NO < 0.02 ppb) at 4 lpm at STP (standard liters per minute (slpm)) is introduced at the center of one wall and sample air is removed at 1 slpm continuously from the opposite wall. The excess zero air is permitted, by design, to exit the chamber at the joint where the chamber rests on the frame and through pinholes in the Teflon film walls of the chamber. Following placement of the chamber on the frame, NO concentrations build up and then stabilize in about 15–30 min, when a steady state is achieved between soil NO emission and the combined removal processes associated with chamber flushing with zero air and deposition to the soil. The net emission flux at the equilibrium mixing ratio is calculated by applying mass balance considerations as follows:

$$F_{NO} = \mu_{NO} Q\{AW_N/[V_m A(60\ \text{s min}^{-1})]\} \qquad (1)$$

where F_{NO} is the net flux of NO in nanograms of N per meter per second, μ_{NO} is the steady state mixing ratio of NO in ppbv, Q is the mass flow of the flush gas in standard liters per minute, AW_N is the atomic weight of nitrogen, V_m is the standard gaseous molar volume, and A is the soil area delineated by a frame in square meters. The gross emission rate within the chamber is calculated by performing standard addition experiments with NO and calculating the NO uptake rate, which is estimated as a first-order loss process [*Williams et al.*, 1988]. Detection of NO is accomplished with a custom-built NO/O_3 chemiluminescence detector that has a detection limit for NO (10 s integration time; signal-to-noise ratio (S/N) = 2) of 5 parts per trillion by volume (pptv). The detection limit for flux depends on the cleanliness of the zero air but is typically 0.010 ng N m^{-2} s^{-1}.

The TVA static chamber technique uses an opaque Teflon-coated aluminum chamber (L × W × H = 76.2 cm × 45.7 cm × 20.3 cm) that is hinged to an aluminum frame driven into the soil [*Valente and Thornton*, 1993]. A channel at the top of the frame is filled with water to seal off the chamber air from the ambient air when the chamber is lowered for a measurement. The chambers are painted white to help reduce heating of the soil when the chambers are down. No zero air is used and the chambers are not flushed. At the beginning of a measurement cycle an ambient air NO reading is taken at chamber height; the chamber then closes automatically, trapping ambient air. The air in the chamber is stirred with a small brushless fan. At 10-min intervals an NO measurement is performed

...ed from the equations shown below, the emission and deposition rates in the chamber are calculated from the increase in NO observed in the chamber. A commercial Thermo Environmental Instruments, Inc. (Franklin, Massachusetts) model 42 NO_x instrument is used by TVA for the NO measurement. At the end of a measurement hour the chamber tops rise and remain up until the next measurement time. TVA measurements are performed every 3 hours, 24 hours a day. The detection limit for flux is typically less than 0.3 ng N m^{-2} s^{-1}.

When a chamber is lowered onto a frame inserted in the soil, the concentration builds up most rapidly immediately after the chamber is lowered. As the concentration builds up in the chamber, the rate of increase slows and approaches a steady state asymptotic value, often referred to as the compensation point, when the emission rate is evidently balanced by the loss term. This observed pattern of NO increase within the chamber can be described well with a model (equation (2)), wherein the net emission rate is governed by a constant gross emission rate term (k_1) and a varying loss term (k_2) proportional to the concentration building up in the chamber.

$$d[\mathrm{NO}]/dt = k_1 - k_2[\mathrm{NO}] \qquad (2)$$

Just after a TVA chamber is lowered, the NO concentration is equal to the ambient level at chamber height (NO_{amb}). Given this initial condition, solving (2) becomes an initial value problem with a first-order differential equation, with the solution given by (3).

$$[\mathrm{NO}](t) = k_1/k_2 + ([\mathrm{NO}_{amb}] - k_1/k_2)e^{-k_2 t} \qquad (3)$$

By fitting the NO versus time curve for each measurement run with a nonlinear regression based on (3), the gross emission rate k_1 and the loss rate k_2 in the TVA chamber are calculated. The net emission rate can then be calculated, if desired, by (2).

Comparison Protocol

A stepwise approach was taken in comparing the two techniques to better understand potential differences in emission rates that might have been found during the study. These comparisons included the most basic elements of the measurement techniques, as well as the overall characterization of the site emissions. To compare calibration sources, the concentration of the NO calibration gases used by the two groups was analyzed using the NOAA instrumentation. To assess the comparability of the two NO analytical systems, including the inlet lines which provided gas samples to the instruments, a common gas sample was simultaneously withdrawn from a common chamber. This test was done using both TVA and NOAA chambers by attaching a tee fitting to the exit port of a chamber. The calculated NO emission rates estimated by both groups for the measurement period (July 6–13) were also compared for the five common soil plots used. Finally, the overall mean emission rates and frequency distributions for NO soil emissions at the site were calculated independently by the TVA and NOAA investigators. All these tests were performed blind with no sharing of data by the groups until all data had been reduced and validated independently.

A field intercomparison of soil NO_x measurement techniques is complicated by at least two significant factors which could introduce undesirable variance external to the measurement systems and data analysis techniques. First, there is considerable spatial variability in emission rates, even on a small spatial scale. For example, using the static chamber technique, *Valente and Thornton* [1993] reported that NO emissions varied by a factor of 3 even on plots as small as 10 m × 10 m with relatively large chambers (each chamber covered 0.28 m^2 of soil). Other investigators have reported even higher variability, as much as a factor of 50 or more, depending on soil homogeneity and fertilizer application technique. Clearly, it is imperative for techniques being compared to sample from the same soil area to the extent possible. This was done several times at five different chamber sites (Figure 1) during the course of the study, since it was possible to insert two NOAA chamber frames side by side within one TVA frame. Two NOAA frames inserted side by side within a TVA frame covered roughly 60% of the area covered by the TVA frame. The second important factor in planning an intercomparison of this type is that a significant diurnal cycle in NO emission rate occurs, with daily peaks as much as 100% or more of the daily minimum. It was not possible to perform measurements from TVA and NOAA chambers on the same area simultaneously, so an effort was made to sample as closely in time as possible and to consider the influence of the diurnal cycle when interpreting the results. All the collocated measurements reported in this paper were performed within 2 hours of one another.

In the discussion of the chamber measurement techniques and in the analysis to follow, a distinction is made between net and gross emission flux. Gross emission flux represents the emission rate from the soil neglecting any depositional losses. Net emission flux represents the difference between gross emission rate and the deposition rate in a chamber. Gross emission appears to be independent of the concentration in a chamber [*Williams et al.*, 1992b]; however, net emission rates decrease as concentrations increase in a chamber, owing to increasing deposition losses at higher concentrations. Therefore when comparing net emission rates from different types of chambers, it is important to reference the net rates to the same chamber concentration. Finally, results were analyzed using regression and analysis of variance techniques to develop an understanding of the comparability of the two techniques.

Results and Discussion

A stepwise approach was taken in the comparison so that in addition to identifying differences in the techniques, the causes of any differences found could be apportioned to the various elements of the measurement and data reduction systems. The first step was to compare the NO calibration gases used by the two groups to calibrate their NO instruments by analyzing samples from both tanks with the NOAA NO instrument (TVA gases were supplied by Scott Specialty Gases, Inc., and NOAA gases were supplied by Scott-Marrin, Inc.). The purpose of this test was to determine whether any relative biases were being introduced by differences in calibration gas sources. The results agreed within 2%, which was similar to the precision of the measurement system and the certification of the standards by the suppliers. We therefore concluded that no significant relative bias was introduced by differences between TVA and NOAA calibration gases.

The next step was to compare the analytical instruments and inlet systems while sampling ambient air trapped in the chambers. This step in the test was strictly a comparison of the transmission of NO through sampling tubing and filters, along with a comparison of the NO analytical instruments used by the two groups; it did not include the calculation of soil NO emission rate. This test would identify any differences caused

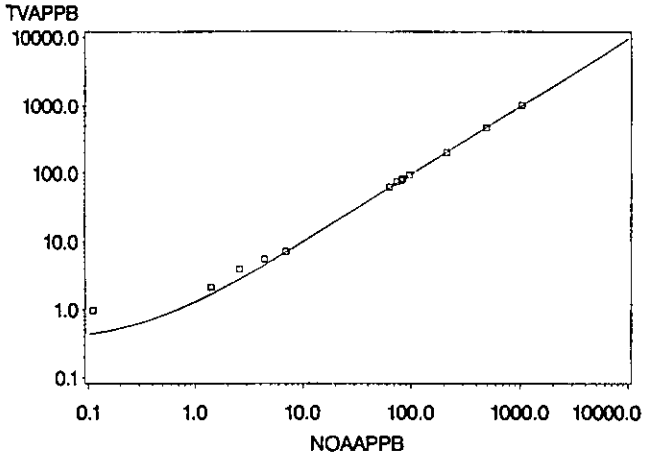

Figure 2. Comparison of TVA and NOAA NO mixing ratio measurements when sampling from common chambers. Data from both TVA and NOAA chambers are shown.

by (1) analytical instruments, (2) moisture or other interferences possibly present in the sample air that could influence either of the two groups' instrumentation differently, and (3) differences in line losses. For this test the TVA and NOAA sample tubes were both connected at a tee at the sampling port on a chamber that was covering the ground, and NO was analyzed independently and simultaneously by the participants. This test was repeated several times with both groups sampling simultaneously from TVA and NOAA chambers. This provided information over a wide range of chamber NO concentrations (over 3 orders of magnitude) typical at this site (and also for many other sites where similar measurements have been made). Figure 2 shows the results of this comparison. The correlation coefficient exceeded 0.99, and the slope of the linear regression line was 0.97. However, the TVA data exhibit an apparent constant 1-ppbv offset until about 10 ppbv NO. The cause of this offset is unknown. The detection limit for the TVA chemiluminescence detector is of the order of 0.1 ppbv, which might contribute some uncertainty to the data at the very lowest levels. Leaks in the sample line were not a problem (i.e., no scatter in the plot), but there might have been some material on the walls of the sample line that contributed to the problem. In any case, because of the curve-fitting routine used by TVA, a constant offset in NO concentration will have very little influence on the calculated flux. The only time when this would be a significant problem is when the ambient air mixing ratio of NO is much less than 1 ppbv, and this rarely occurred at this site owing to the nearby Muscle Shoals/Florence urban areas. This comparison indicated that the instruments and inlet lines used by the two groups are essentially equivalent in measuring NO from actual chamber air at NO levels greater than 1 ppbv. However, this test does not show how differences in the methods used by the groups to operate the chambers and calculate the NO emission rates influence the flux measurements. For this step of the comparison we turn our attention to collocated and simultaneous (or nearly so) measurements of the soil NO emission rates of the two groups.

Figures 1a and 1b show the five TVA chamber locations (T1A, T3, T4, T4A, and T5) where two NOAA frames (N9A and N10A, N13 and N14, N9 and N10, etc.) were mounted within the TVA frame. For comparison, the TVA and NOAA NO flux measurements on common plots were based on the net emission rates, using the concentration in the NOAA chambers as a reference value. Since differences in calibration gases, NO analysis instruments, and line losses were shown to be insignificant, any differences found at this level are expected to be due to differences other than those listed above. These potential sources of error relate to the operation of the chamber or the technique used to calculate the flux, or differences related to the fact that strictly simultaneous measurements were not possible and that the soil areas are not exactly the same (two NOAA frames enclosed roughly 60% of the area of one TVA frame). In the first case, differences in chamber operation such as stirring rate, dry zero air flush (NOAA), wall losses, chamber geometry, etc., may influence the calculated emission rate. Furthermore, differences in the way in which these fluxes are calculated, i.e., TVA using curve fitting and NOAA using a mass balance approach, may result in differences. The second area of consideration, that of nonsimultaneous sampling, relates to the fact that strictly identical soil areas were not sampled and real-time concurrent sampling was not possible. Despite these considerations that could cause sampling biases, our results show very good agreement.

Figure 3 shows the results of the NO flux comparison for common plots. Linear regression on this data set yields a correlation coefficient of 0.98 and a slope of 0.97. A paired t test performed on these collocated chamber measurements indicates that the mean difference between the two techniques is not statistically different than zero ($t = 0.1918$ with 25° of freedom, and the mean difference was 0.16 ng N m^{-2} s^{-1}, with the TVA values averaging slightly higher than the NOAA values). We have carefully examined the four or five data points at the low end (1–10 ng N m^{-2} s^{-1}) to determine why they are farther off the one-to-one line than the rest of the points. We could find nothing unique or peculiar other than that these data were not nearly as simultaneous as the bulk of the data. Also, occasionally, the two simultaneous NOAA data points differed substantially (by a factor of 3 or greater), while the average of the two agreed very well with the corresponding TVA flux data point. Considering all the potential sources for differences and the fact that the chambers could not be perfectly collocated and precisely simultaneous in operation, these results are very satisfactory. We conclude that the TVA and

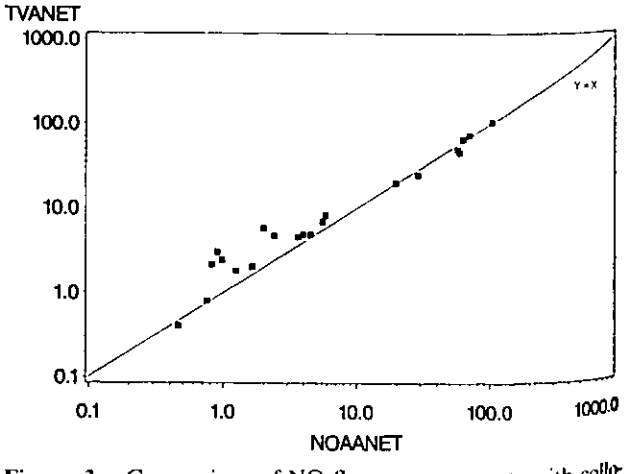

Figure 3. Comparison of NO flux measurements with collocated TVA and NOAA chambers. Data are expressed in nanograms of nitrogen per square meter per second.

Table 1. Summary of TVA Static Chamber Soil NO Emission Data

Plot Number	Mean	Standard Deviation	Range	Number of Points
July 6 Through July 13, 1992				
	28.0	27.7	<0.3–98.0	29
	52.2	23.8	20.1–111	22
	6.44	3.93	<0.3–14.8	52
	4.07	2.52	<0.3–9.9	52
	4.65	3.57	0.9–11.6	30
	49.4	24.7	25.3–119	22
	3.02	1.72	<0.3–6.0	51
average	17.7	20.6	3.02–49.4	6
average	15.1	22.5	<0.3–111	258
July 15 Through July 23, 1992‡				
	36.7	47.3	<0.3–176	64
	50.9	59.9	<0.3–252	61
	3.09	3.70	<0.3–16.8	58
	5.16	4.67	<0.3–21.5	65
	6.05	8.39	<0.3–34.7	57
average	20.4	22.0	3.09–50.9	5
average	21.1	39.7	<0.3–252	305

averages give equal weight to all chamber sites, and data aver- give equal weight to all measurements.
and T1A represent data from the same location segregated into me periods. (See Figure 1 for details.)
T4 and T4A represent data from a chamber that was moved to two different locations.
All five TVA chambers shifted by 2 m.

Table 2. Summary of NOAA Dynamic Chamber Soil NO Emission Data During the Intercomparison Period From July 6 Through July 13, 1992

Plot Number	Mean	Standard Deviation	Range	Number of Points
N1	1.65	1.56	0.4–6.1	11
N1A	39.8	13.9	23.1–53.3	5
N2	160	77.3	58.1–305	10
N2A*	77.6	44.8	33.8–152	5
N3	1.72	0.42	1.1–2.5	13
N4	0.85	0.32	0.4–1.4	14
N5	0.90	0.23	0.6–1.3	8
N6	1.14	0.47	0.5–2.1	10
N7	11.6	4.40	5.1–19.1	15
N8	15.9	15.4	6.1–53.9	12
N9	2.62	1.37	1.1–4.8	6
N9A	45.8	30.7	18.6–81.0	5
N10	1.95	1.86	0.4–4.5	6
N10A	38.1	18.8	20.4–56.9	4
N11	2.02	1.37	0.2–4.3	8
N12	1.89	1.19	0.7–3.7	8
N13	2.85	2.43	0.7–5.7	5
N14	3.55	2.57	0.9–6.2	4
Plot average	18.0	33.3†	0.85–133‡	17
Data average	20.6	46.8	0.2–305	148

*Same location as plot 2; data taken after July 10, 1992, 1500 CDT.
†This value is the standard deviation of the chamber means in the first column after combining the data for N2 and N2A (same plot).
‡This value is from combined N2 and N2A (same plot).

VA systems are equivalent in their measurement of NO emission flux.

Finally, we assess the comparability of the techniques in characterizing the overall emissions from a site. At this level, spatial variability and siting criteria can influence significantly the comparison between techniques. This is of particular interest because it is known that the spatial variability in emission rates is often disconcertingly high; nevertheless, it is desirable to make the best possible areal estimates given the logistical realities of keeping chamber size and numbers manageable. Tables 1 and 2 present comparisons of the statistics on NO emission derived from the two groups. Items T1 through T10 in Table 1 are the TVA plot locations used during the intercomparison between the TVA and NOAA techniques (see Figure 1) and are referred to as TVA-A. Plot locations T6 through T10 in Table 1 are referred to as TVA-B and were later used by TVA after the intercomparison, July 15–23, 1992, where each new location was about 2 m away from an old plot position. These data show substantial similarity in the characterization of the mean emission rate by plot for the entire site. The plot mean values and associated standard deviations during the intercomparison for TVA-A and the NOAA chambers are 17.7 (20.6) and 18.0 (33.3) ng N m^{-2} s^{-1}, respectively. During the week following the intercomparison the shifted TVA-B chambers gave values of 20.4 (22.0). As noted previously, if only the collocated chambers are considered then the agreement between the TVA mean and NOAA mean (difference is 0.16 ng N m^{-2} s^{-1}) is even closer but with the TVA data slightly higher. In reviewing these overall comparisons, it should be noted that over 70% of the NOAA measurements were made during daylight hours, while TVA measurements were evenly divided between day and night. Since NO emissions show diurnal variation (higher soil temperature yields greater flux), it is useful to also compare the results separated into day and night measurements (Table 3). The total soil areal coverage was similar at each subsite (5 TVA chambers covered 1.45 m^2 and 14 NOAA chambers covered 1.2 m^2). Coefficients of variation were higher for NOAA (227%) than TVA (149%, TVA-A and 188%, TVA-B), probably owing to the smaller NOAA chamber size. Recent results investigating the effect of chamber size on soil gas emission rates have also shown greater variability associated with smaller chamber size [*Ambus et al.*, 1993]. At this site the deposition losses in the chambers were found to be rather small. The TVA data indicated that deposition losses ranged from near zero to about 3% min^{-1}. The NOAA NO uptake data exhibited a large variability, including some negative values. Table 4 shows those values with the highest degree of reliability but, even so, the two values greater than 0.1 cm s^{-1} are much higher than expected. The mean value without these two apparent outliers is 0.028 cm s^{-1}, which is equivalent to a loss term of almost 5% min^{-1} and is consistent with the TVA data. This means that at this site the differences between the net and gross emission rates tended to range from near 0 to about 25%.

Table 3. Comparison of Day (0600–1800 CDT) Versus Night (1800–0600 CDT) Mean Data

Parameter	NOAA	TVA
Day emission rate, ng N m^{-2} s^{-1}	24.6	17.5
Night emission rate, ng N m^{-2} s^{-1}	10.4	11.1
Day soil temperature, °C	34.7	32.8
Night soil temperature, °C	26.5	27.9

Table 4. Loss Terms Calculated From NOAA Uptake Experiments

Loss Term, cm s^{-1}	NO Mixing Ratio, ppbv	Soil Temperature, °C	Plot Number
0.175	2.8	33	3
0.047	2.8	34	1
0.003	18.4	41	7
0.006	19.7	40	8
0.057	3.7	38	3
0.014	0.98	42	4
0.041	1.7	36	5
0.189	1.1	40	6
0.013*	2.1	33	4

*Standard addition test; all others are flow variation tests.

Conclusions

These findings indicate that data sets collected with a zero air–flushed dynamic chamber technique and a static chamber method are comparable and may be combined without major concern for differences in technique. Furthermore, while more studies should be conducted, these results suggest that other investigators using similar techniques may also compare data successfully. This information is useful as investigators move toward combining their data sets to improve the inventory of soil NO emissions.

This study also has shown that the techniques used by each group in attempting to characterize the site yield remarkably similar results despite differences in chamber size, plot location, extent of areal coverage, and random error associated with the measurements. This finding, as is the case for the confirmation that the techniques give similar results, is significant in that it also means that field data used to characterize emissions estimates by both protocols can be pooled to better estimate regional soil NO emissions inventories. This information will aid in the development of databases needed in modeling regional ozone production and transport. The stepwise protocol taken in this intercomparison proved to be very useful in establishing the comparability of all important aspects of the measurement systems being studied, and we recommend a similar approach to other investigators conducting comparisons in the future.

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References

Ambus, P., H. Clayton, J. R. M. Arah, K. A. Smith, and S. Christensen, Similar N_2O flux from soil measured with different chamber techniques, *Atmos. Environ.*, *27*, 121–123, 1993.

Graham, J. A., et al., Direct health effects of air pollution associated with acidic precursors emissions, in Acidic Deposition: State of Science and Technology, *NAPAP SOSIT Rep. 22*, vol. 3, Natl. Acid Precip. Assess. Program, Washington, D. C., 1990.

Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hubler, and P. C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distribution, *J. Geophys. Res.*, *92*, 4191–4207, 1987.

Logan, J. A., Nitrogen oxides in the troposphere: Global and regional budgets, *J. Geophys. Res.*, *88*, 10,785–10,807, 1983.

Shriner, D. S., W. W. Heck, S. B. McLaughlin, D. W. Johnson, P. M. Irving, J. D. Joslin, and C. E. Peterson, Response of vegetation to atmospheric deposition and acidic precipitation, in Acidic Deposition: State of Science and Technology, *NAPAP SOSIT Rep. 18*, vol. 3, Natl. Acid Precip. Assess. Program, Washington, D. C., 1990.

Valente, R. J., and F. C. Thornton, Emissions of NO from soil at a rural site in central Tennessee, *J. Geophys. Res.*, *98*, 16,745–16,753, 1993.

Williams, E. J., and E. A. Davidson, An intercomparison of two chamber methods for the determination of emission of nitric oxide from soil, *Atmos. Environ.*, *A27*, 2107–2113, 1993.

Williams, E. J., D. D. Parrish, M. P. Buhr, and F. C. Fehsenfeld, Measurements of soil NO_x emissions in central Pennsylvania, *J. Geophys. Res.*, *93*, 9539–9546, 1988.

Williams, E. J., A. Guenther, and F. C. Fehsenfeld, An inventory of nitric oxide emissions from soils in the United States, *J. Geophys. Res.*, *97*, 7511–7520, 1992a.

Williams, E. J., G. L. Hutchinson, and F. C. Fehsenfeld, NO_x and N_2O emissions from soil, *Global Biogeochem. Cycles*, *6*(4), 351–388, 1992b.

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