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Intercomparison of ground-based NO_y measurement techniques

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Abstract. An informal intercomparison of NO_y measurement techniques was conducted from June 13 to July 22, 1994, at a site in Hendersonville, Tennessee, near Nashville. The intercomparison involved five research institutions: Brookhaven National Laboratory, Environmental Science and Engineering, Georgia Institute of Technology, NOAA/Aeronomy Laboratory, and Tennessee Valley Authority. The NO_y measurement techniques relied on the reduction of NO_y species to NO followed by detection of NO using O₃-chemiluminescence. The NO_y methods used either the Au-catalyzed conversion of NO_y to NO in the presence of CO or H₂ or the reduction of NO_y to NO on a heated molybdenum oxide surface. Other measurements included O₃, NO_x, PAN and other organic peroxy-carboxylic nitric anhydrides, HNO₃ and particulate nitrate, and meteorological parameters. The intercomparison consisted of six weeks of ambient air sampling with instruments and inlet systems normally used by the groups for field measurements. In addition, periodic challenges to the instruments (spike tests) were conducted with known levels of NO, NO₂, NPN, HNO₃ and NH₃. The NO_y levels were typically large and highly variable, ranging from 2 ppbv to about 100 ppbv, and for much of the time was composed mostly of NO_x from nearby sources. The spike tests results and ambient air results were consistent only when NO_x was a substantial fraction of NO_y. Inconsistency with ambient air data and the other spike test results is largely attributed to imprecision in the spike results due to the high and variable NO_y background. For the ambient air data, a high degree of correlation was found with the different data sets. Of the seven NO_y instrument/converters deployed at the site, two (one Au and one Mo) showed evidence of some loss of conversion efficiency. This occurred when the more oxidized NO_y species (e.g., HNO₃) were in relatively high abundance, as shown by analysis of one period of intense photochemical activity. For five of the instruments, no significant differences were found in the effectiveness of NO_y conversion at these levels of NO_y with either Au or Mo converters. Within the estimated uncertainty limits there was agreement between the sum of the separately measured NO_y species and the NO_y measured by the five of the seven techniques. These results indicate that NO_y can be measured reliably in urban and suburban environments with existing instrumentation.

1. Introduction

In order to understand the many and varied chemical pathways in the atmosphere an extremely diverse and large number of compounds must be measured, many at very low

concentrations. One important family of compounds that plays a key role, directly or indirectly, in almost all of photochemical processing are the oxides of nitrogen. Members of this group act as catalysts for photochemical production of ozone (O₃) [Liu *et al.*, 1987; Lin *et al.*, 1988; Trainer *et al.*, 1993, 1995]; they regulate the oxidative capacity (hence, cleansing ability) of the atmosphere [Levy, 1972]; and they are responsible for a significant fraction of acid deposition [Irving, 1991].

A number of measurement methods for the principal nitrogen oxide species (NO and NO₂, together called NO_x), peroxyacetic nitric anhydride (PAN), and nitric acid (HNO₃) are available and have been critically evaluated [Hoell *et al.*, 1987; Fehsenfeld *et al.*, 1990; Roberts, 1990; Anlauf *et al.*, 1985; Fox *et al.*, 1988]. There are also techniques available for the determination of total reactive nitrogen oxides (NO_y) in the atmosphere [Fahey *et al.*, 1986; Atlas *et al.*, 1992; Parrish *et al.*, 1993; Sandholm *et al.*, 1994; Nielsen *et al.*, 1995]. Depending on proximity to sources, altitude, and other factors NO_y will consist of NO, NO₂, NO₃, N₂O₅, HNO₂, HNO₃, HNO₄, PAN and its analogs, nonperoxy organic nitrates, halogen-nitrogen species such as ClONO₂ and BrONO₂, and particulate nitrate (NO₃). This is an important measurement since it

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provides a means to assess, from a mass balance approach, whether or not the individually measured species account for all of the nitrogen oxides in a particular air mass. If a deficit in NO_y is found, then there are two distinct possible causes: (1) that the measurements are in error, or (2) that there are unmeasured nitrogen oxide compounds in the atmosphere. It is this latter, more interesting, case that makes the determination of NO_y in the atmosphere so desirable since it may provide another probe into the complex photochemistry.

Measurement methods for NO_y all rely on metal-surface promoted reduction of the more highly oxidized species to NO which is determined via chemiluminescence or laser-induced fluorescence. However, there are differences among current NO_y measurement techniques. One principal difference is in the metal catalyst used to effect reduction to NO; currently two metals are in widespread use: gold and molybdenum. There are also differences in how these metals are employed in practice. For example, Au is generally employed as a tube of pure metal used in conjunction with either carbon monoxide (CO) or hydrogen (H₂) gas as reductant while Mo is employed as an oxide (generically, MoO) in mesh form with no additional gases. Also, the Au tube converter has been specifically designed to convert only gas-phase species [Fahey *et al.*, 1985] and to pass the majority of the aerosol component in the air sample; typical MoO converters in use currently are purposefully designed to respond to aerosol nitrate. The inlet systems used to introduce the atmospheric sample into the metal converter are also very important since some of the NO_y species are susceptible to significant loss on surfaces. Long unheated inlet lines upstream of the heated converter are expected to produce significant losses of species such as HNO₃.

Unfortunately, from both analytical and practical viewpoints, the determination of NO_y is an inherently difficult measurement since an entire suite of species is being measured, not a single compound. The efficiency with which the different NO_y species are converted to NO is of paramount importance because when conversion for all NO_y compounds is not close to unity the measurement becomes highly uncertain. Further, it is also necessary that no non-NO_y species be converted. Non-NO_y species include ammonia (NH₃), organic amines, nitriles, and nitrous oxide (N₂O). The environment in which the NO_y measurements are to be conducted also must be considered. During aircraft missions dramatic and rapid fluctuations in NO_y and in environmental factors, such as pressure and water vapor levels, are routinely experienced. These rapidly changing conditions can significantly influence the efficiencies of converters [Crosley, 1996]. The relative importance of interferences (non-NO_y species such as HCN and NH₃) also changes with environment. For example, HCN is relatively uniform in the troposphere at ~160-170 pptv and may be converted to NO with efficiencies that range from <2% to ~100%, depending on conditions [Fahey *et al.*, 1985; Kliner *et al.*, 1997]. This presents very little interference to ground-based measurements where NO_y levels are in the low ppbv range, but may be as much as 100% interference in the middle to upper troposphere. Thus in order to assess the confidence that can be placed in NO_y measurement data, critical evaluation of these measurement methods is necessary. Extensive laboratory studies of the utility of the Au tube converter have been carried out by Fahey *et al.* [1985] and by Kliner *et al.* [1997], although results from the latter study can not readily be applied to ground-based studies such as reported

here. Only one similar study for the Mo converter has been published [Nunnermacker, 1990].

Perhaps the most effective means to evaluate the performance of different NO_y measurement techniques is comparison of data collected simultaneously while the instruments are collocated and measuring under actual field conditions. However, only one ground-based intercomparison of NO_y techniques has been done [Fehsenfeld *et al.*, 1987]. Two instruments were involved in that study, and both used NO-O₃ chemiluminescence as the analytical technique. One instrument used an Au tube heated to 300°C with added CO, while the second instrument used Mo mesh heated to 400°C. Both instruments produced similar measurements of NO_y in ambient air ranging between 0.5 ppbv and 60 ppbv. Since those results were published no other ground-based comparisons of NO_y instruments have been reported.

This paper describes results from an extensive ground-based NO_y instrument intercomparison conducted near Nashville, Tennessee, during June and July of 1994. This experiment was sponsored by the Southern Oxidants Study (SOS) in preparation for a field program involving a large number of ground- and aircraft-based NO_y instruments in Nashville during the summer of 1995. Because of differences in those NO_y instruments, it was thought necessary from the standpoint of data comparability to evaluate those same instruments ahead of time. Since results from an earlier (1992) SOS-sponsored study in Atlanta indicated significant degradation of NO_y converters used in that urban environment, it was considered prudent to conduct this comparison in the same locale as the upcoming 1995 field study to determine if similar problems would result. Therefore, during June and July of 1994, representatives from five separate laboratories involved in the SOS program brought their NO_y instruments to a site near Nashville, Tennessee, for six weeks of simultaneous measurements.

2. Experiment

This intercomparison was open and informal in nature. This format was chosen to minimize the potential of data being lost from an instrument due to catalyst poisoning, as was the case with a previous experiment. However, while exchange of scientific and technical information and interaction among investigators during the experiment was allowed, free exchange of ambient data and spike results was discouraged. The measurements were made using separate inlets for each instrument (i.e., there was no common sampling manifold). These inlets were intended to be the same as or at least similar to the inlets used by the groups in sampling during the field campaign the next year.

2.1. Site Location

The measurements took place in Hendersonville, Tennessee, which is a suburb 20 km to the northeast of Nashville. There were a number of strong local sources of NO_x, including heavily traveled highways, coal-fired power plants, and the outflow of pollution from the Nashville metropolitan area. An additional, unexpected, source of pollution during this experiment was a biomass burning operation that was located ~1 km to the south and east of the site. Burning was conducted during the entire summer to remove dead trees and other vegetation resulting from severe ice storms the previous winter and spring. There were also very strong regional

sources of pollutants from coal-fired power plants 20 km to the east (Gallatin, Tennessee) and 100-120 km to the west and north (Johnsonville, Tennessee; Cumberland, Tennessee; Paradise, Kentucky). Because the nearby sources were so significant, during much of the measurement period a large fraction of NO_y was in the form of NO_x which did not provide a stringent test of the NO_y converters. On the other hand, the many local emission sources were expected to challenge the ability of the converters to remain effective in an urban environment for the four to six week duration of the study. Since this site had already been chosen as the principal ground-based measurement site for the 1995 study, it was necessary that the intercomparison take place there.

The site proper was a large open field in a rural residential area west of Hendersonville. The field was surrounded on all sides by tall (15-20 m) trees, but the open area was large enough that the cluster of research trailers and vans was well away (>100 m) from any nearby canopy. The field was used by the owner for growing grass which was periodically mowed. In addition, there was a small barn and small field nearby where the owner maintained 5-10 head of cattle. Since this was considered a significant source of ammonia, which can be an interference in the NO_y measurement, testing for this compound was included in the intercomparison protocols. There also was a lightly-traveled two-lane road due west of the site and a small number of residences nearby.

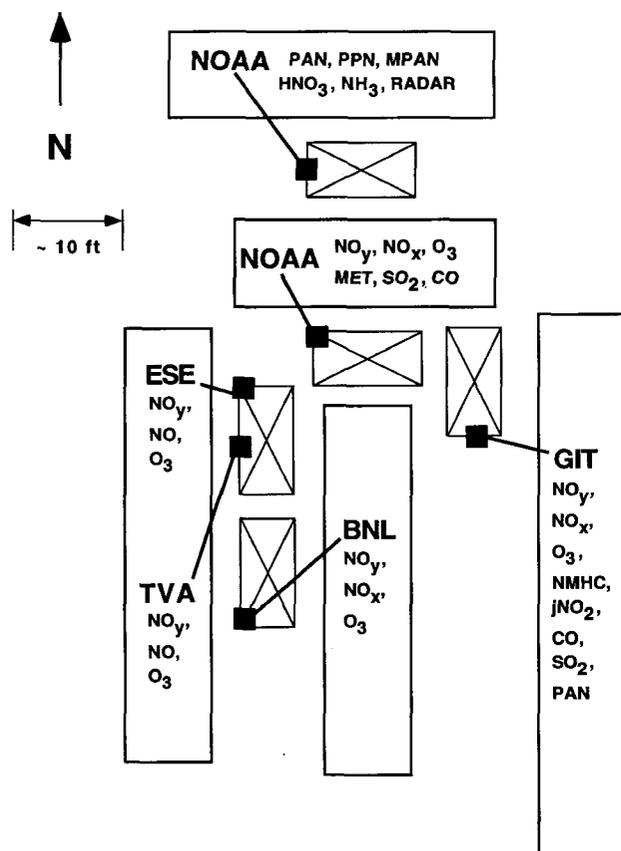


Figure 1. Plan view of the mobile research facilities and sampling towers used during this study. There were four trailers (GIT; ESE/TVA; NOAA; NOAA) and one motor home (BNL). The heavy solid squares show the locations of the NO_y inlet systems that were placed on scaffold towers used during the measurements.

2.2. Site Meteorology

The prevailing surface wind direction during the measurement period was generally southwest and brought air from the Nashville metropolitan area. Indeed examination of outflow air from Nashville was one reason that this site was chosen for the 1995 SOS intensive study. These air parcels were typically laden with pollution from automobile exhaust emissions which contain high levels of CO and NO_x. In contrast, winds from the east and northeast brought air masses rich in coal-fired power plant emissions which contain high levels of SO₂ and NO_x. Additionally, wind from the east and southeast caused an increase in visible smoke at the site which came from the nearby city landfill where dead vegetation was being burned. In a few instances large amounts of airborne ash were observed from the tops of the sampling towers. There were only one or two periods during the measurements when the wind was from the northwest. Air from this sector provided the lowest levels of trace species that were measured during the campaign, although significant sources of NO_x (Paradise and Cumberland power plants) are present at about 100-150 km in that direction.

The maximum temperature recorded was 33°C with an average of 26°C. Dew point temperatures were typically in the low to mid 20°C range, and the relative humidity averaged around 80%. A good deal of precipitation fell during the measurements, mostly as a result of thunderstorm activity. During June frontal passages from the northwest were the principal weather influences. During early July, tropical storm Alberto moved onshore from the Gulf of Mexico into Georgia, and by the middle of July a stationary front had set up just to the north of Nashville. These factors resulted in high relative humidity, increased cloudiness, and almost daily rainfall at the site.

2.3. Site Layout

The different laboratories participating in the instrument intercomparison provided their own mobile facilities (total of four trailers and one recreational vehicle) for housing the instrumentation. Two groups shared one trailer, and there was a separate trailer that housed the additional measurements necessary for the experiment. In order to locate the sampling inlets close together to avoid possible biases due to sampling different air parcels, the mobile laboratories were parked in the arrangement shown in Figure 1. However, due to other considerations of access to outside trailer panels, walkways between trailers, sampling line lengths, and the need to provide sufficient room for the sampling towers (see below), the location of the sampling inlets was not as close together as initially hoped. In retrospect, this did not appear to bias the NO_y data.

Sampling towers were built of standard construction scaffolding where the uppermost common platform height was approximately 8 m above ground. This was a reasonable compromise between the height required to reduce effects from the local tree canopy (i.e., sampling the undisturbed atmospheric air flow) and the safety considerations of personnel climbing the structures. The NO_y sampling inlets were then mounted to these towers at a common height of 9 m above ground level. The locations of the different inlets are shown in Figure 1. Although the company providing the scaffolding was asked to supply the cleanest equipment possible (i.e., free of oils, greases, and other construction

materials), the materials provided had all been freshly painted. The paint odor was noticeable for several days.

2.4. NO_y Instrumentation

Five different laboratories were involved in the experiment. Each of the groups provided all the necessary equipment and instrumentation that they would normally use for field measurements, including the inlet systems normally used. Personnel from the Aeronomy Laboratory were given the responsibility of designing and organizing the experiment and acted as coordinators for the ambient sampling and spike tests.

2.4.1. Brookhaven National Laboratory (BNL). The BNL three-channel research-grade instrument was designed for aircraft deployment but was used for this ground-based experiment after some minor changes were made to the instrument configuration (see Figure 2). The protocol for instrument operation was similar to that used previously [Kleinman *et al.*, 1995]. Chemiluminescence via reaction with O₃ was used for the selective determination of NO after conversion of NO_y to NO using a hot metal catalyst. The NO_y converter was a Pyrex tube (2.5 cm OD x 10 cm) loosely packed with ~15 g of molybdenum screen (40 x 40 wires cm⁻¹) and heated to 350°C at ambient pressure. A 60-μm, stainless-steel frit downstream of the converter prevented contamination of the mass flow controller. An unheated PFA Teflon tube (~30 cm from tip to heated Mo) was the common inlet for the three

instrument channels. This tube was longer than usual to accommodate standard additions during the intercomparison. The total flow through this inlet was 3 L min⁻¹ (at STP, standard liters per minute (slpm)). The NO_y converter was located in a small shaded container at the top of the sampling scaffold along with the mass flow controllers for all three channels. Routine standard additions in ambient air, periodic calibrations in zero air, and intercomparison standard additions were all done at the common instrument inlet. The multiple tubes connecting the three channels and calibration valves with the analyzer located in the mobile laboratory below were routed through an opaque outer sleeve with an exhaust fan at the bottom to pull ambient cooling air over the lines.

The basic converter design used in this instrument has been tested for conversion efficiency with NO₂, HNO₃, NH₃, hydrogen cyanide (HCN), organic nitriles (RCN), and organic nitrates [Nunnermacker, 1990]. The converter used here had been changed slightly in that the Pyrex tube was now centered within an outer ceramic sleeve which was wound with heating wire rather than directly wrapped onto the tube itself. The thermocouple sensor was cemented to the surface of the Pyrex tube. This configuration provided for more even heating of the converter and eliminated "hot spots" which cause the molybdenum to slowly decompose. When required due to lost efficiency, the standard operating procedure for this instrument provides for converter bakeout under nitrogen at 450 - 500°C. No conversion efficiency degradation was observed during this program (efficiency for NO₂ was consistently 98±1%), even with the large burden of smoke and soot periodically encountered, thus bakeout was not required.

Photon counting was used to acquire the signal. Instrument zeros were performed by diverting the sample flow through a 1-L mixing vessel (pre-reactor) in the O₃ line every 4 hours for 5 min. Linear interpolation was used between the zeros (with a typical magnitude of 120 Hz) to calculate the net ambient signal. A standard addition of NO was applied every 2 hours for 5 min. The measured instrument response was also verified periodically by multi-point calibrations in zero air. The sensitivity to NO was ~0.4 Hz pptv⁻¹ which yields a theoretical detection limit for NO of ~50 pptv for a 1-s integration time at signal to noise ratio (S/N) of 2. In practice the detection limit was compromised by drift in the background zero. A standard addition of NO₂ was also applied every 2 hours for 5 min to verify the conversion efficiency of the Mo converter. In each case, the average of the last 3 min of each mode was used as the level for that period. For standard additions, the averages of the ambient measurements 3 min before and after the standard addition were used. During calibrations in zero air a signal in the NO_y channel (i.e., artifact) was noted and calculated as the response for zero air above the pre-reactor zero. This was typically less than 300 pptv. Because the artifact changed with each cylinder of zero air, it was judged to be primarily an unknown contaminant and was neglected in ambient measurements. For this ground-based operation, data were recorded at 15-s resolution and 1-min averages were used for data processing. We estimate the uncertainty of this NO_y measurement to be the greater of ±10% or ±50 pptv for the 1-min data. The factor of 10% appears due to diurnal changes in water vapor concentration.

2.4.2. Environmental Science and Engineering (ESE). NO_y was measured via conversion to NO with a commercially available converter consisting of Mo metal

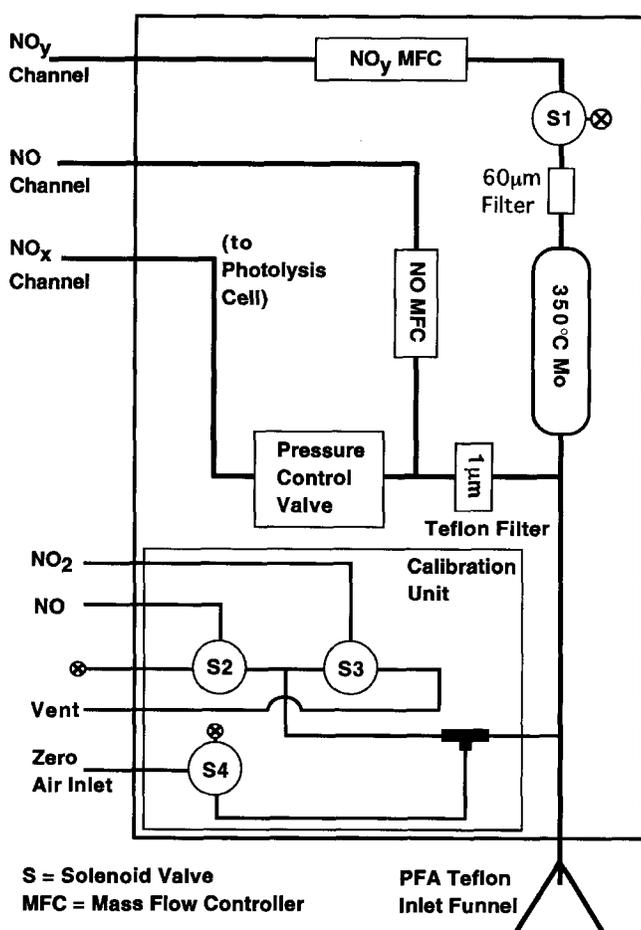


Figure 2. Schematic diagram of the BNL NO, NO_x, and NO_y inlet housing.

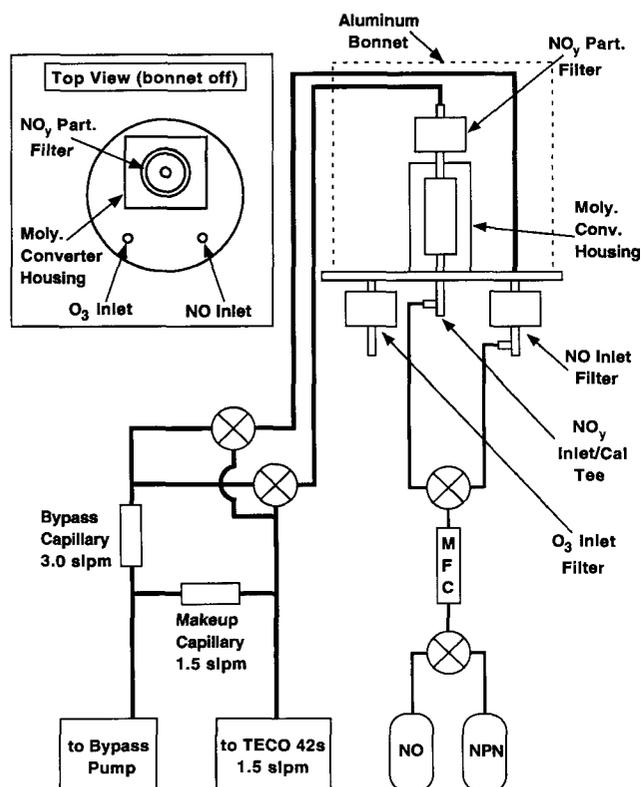


Figure 3. Schematic diagram of the ESE O₃, NO, and NO_y inlet. MFC, mass flow controller.

mesh heated in a stainless steel housing. The resulting NO was determined via NO-O₃ chemiluminescence with a modified commercial NO-NO₂-NO_x monitor (model 42S; Thermo Environmental Instruments, Inc. (TEII), Franklin, Massachusetts). The instrument inlet design is shown in Figure 3. The converter was temperature-controlled at $375 \pm 3^\circ\text{C}$ and housed inside an inverted aluminum bonnet with a bottom plate for mounting to the sampling tower (~ 9 m). A stainless steel converter inlet tube (0.6 cm OD x 7.5 cm) protruded through the plate only far enough for a Teflon tee to be attached for introduction of calibration gases. Separate inlets for an O₃ analyzer and the NO channel of the TEII 42S also protruded from the bonnet. Both inlets were connected to 47 mm Teflon filter packs which were located >15 cm from the NO_y inlet to reduce local surface losses of HNO₃. Another filter was placed in the NO_y sample line downstream of the converter to protect the analyzer from MoO dust. The instrument was plumbed to provide constant (~ 3.5 L min⁻¹) flow rates through both the NO and the NO_y inlets. The TEII 42S instrument collected and stored in memory three different signals by sampling at 10-s intervals from (1) a prereactor cell, (2) the NO inlet, and (3) the NO_y inlet with the Mo converter. When sampling through the prereactor cell, the instrument measured a background signal (0.3 - 0.8 ppbv equivalent NO; mostly dark current from the phototube) which was subtracted from the NO and NO_y signals. The net NO and NO_y signals were then output to a data logger. As a result, the 1 min average data values were actually the average of two 10 s periods separated by 20 s within each minute. The data logger also controlled all the automated calibration sequences during the study.

Conversion efficiency of the Mo converter was checked daily via addition of an ESE-provided NPN standard gas (calibrated before and after the study) into the NO_y inlet and was found constant at 80-85%. Thus there was no significant degradation in conversion efficiency during this study.

Periodic (every 8 hours) standard additions of NO were used to calibrate the NO and NO_y channels during the intercomparison, and calibration curves were determined at the beginning and end of the study via gas replacement to confirm instrument linearity across the sampling range. For the standard addition calibrations, the ratio of the instrument output (directly in ppbv) to the calculated mixing ratio of the added standard (in ppbv) was used as the response factor of the instrument. The instrument response to the standard was determined by taking the difference between the 5-min average during the calibration and a 5-min average either immediately before or after the calibration. This approach reduced the effect of the highly variable atmospheric NO_y concentrations on the precision of the calibration results. All raw data values were subsequently divided by the overall averaged response factor. The NO_y-channel response of the instrument remained virtually constant throughout the six week study at 85% with relative standard deviation (RSD) of 9.0%. The NO-channel response was, on average, about 5% lower than the NO_y-channel response (RSD of 4.6%), which agrees well with the theoretical homogeneous loss of NO from O₃ titration in the sample line. The NO-channel RSD is an indication of the precision of the NO-O₃ chemiluminescence detection of NO while the NO_y-channel precision combines the uncertainty of the NO detection with uncertainties introduced by the presence of the Mo converter (i.e., larger and more variable NO_y background). Total uncertainty for the NO_y measurement is estimated at $\pm 20\%$ for accuracy and $\pm 20\%$ for precision.

2.4.3. Georgia Institute of Technology (GIT). The measurement of NO_y was made by the conversion of NO_y to NO with custom built MoO converters. The NO produced by the conversion process was subsequently measured by a TEII model 42S NO-NO_x chemiluminescence instrument. The instrument inlet design, shown in Figure 4, accommodated three sample inlets: two were used for NO_y measurements and the third was used for the measurement of NO. Two different MoO converters were used during the study. The first converter was a 1.2 cm OD MoO tube with a wall thickness of 0.15 cm. The second converter was a 1.2 cm OD quartz tube filled with MoO shavings. Both tubes were 30.5 cm in length and each tube was placed in a commercially available oven (Model 2-3802, Supelco, Inc.) that was controlled at a constant 390°C by separate temperature controllers (Model CN76000, Omega Engineering). For this study, data are reported only from the MoO tube converter, to which an unheated inlet line (~ 60 cm X 0.6 cm OD PFA Teflon tube) was connected. Sample flow was controlled at 1.0 slpm. The three inlets were connected to a six-port multi-position valve (4 inlets, 2 outlets; Model SC4P, Valco Instruments Co.). This valve allowed sampling from one port while all other ports were common-connected to a purge pump which provided continuous air flow through all nonsampling inlets. The valve timing was controlled via TTL outputs from a data acquisition/control computer running a commercially available software package (Labtech Notebook Pro, Laboratory Technologies Corp.) The timing loop consisted of 5 min sample times for each of the measured species, NO_{y,1}, NO_{y,2} and NO. The internal TEII instrument timing cycle for calculating background values alternated

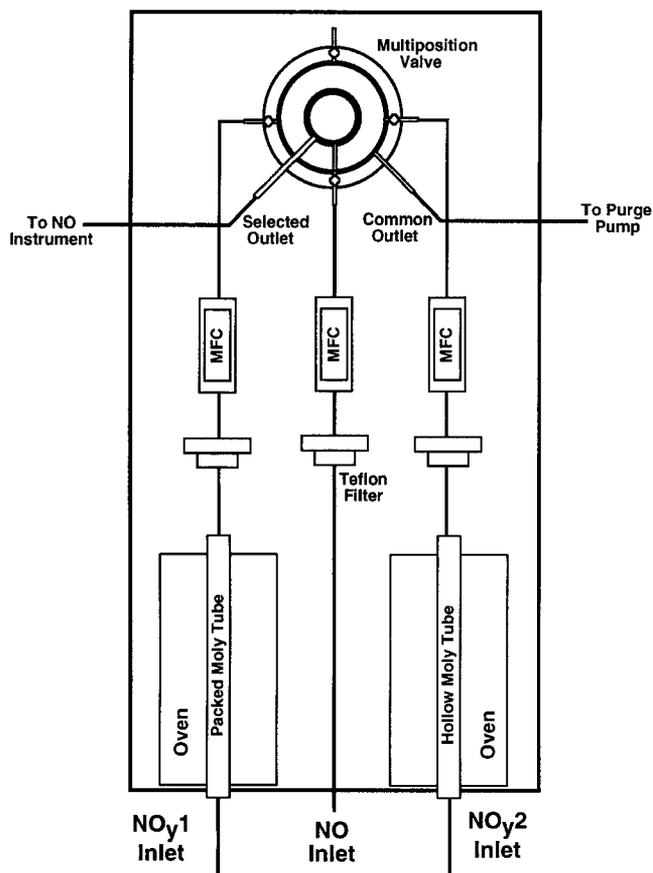


Figure 4. Schematic diagram of the GIT NO and NO_y inlet. MFC, mass flow controller.

every 10 s between sample and background modes. No modifications were made to this timing cycle. Analog output from the TEII was sampled at 1 Hz and the average of 10 samples was then saved. Calibration and NO_y conversion factors were applied to the data and 1 min averages were made of the final data.

Calibrations were routinely conducted with calibration gases of NO in N₂ and NO₂ in N₂, (Scott Specialty Gases). The gases were dynamically diluted with zero air to the proper concentration. Two different types of calibration methods were used. The first was gas substitution, where an excess amount of known calibration gas was sent to the converters. This type of calibration was conducted approximately every three days. The second method was the standard addition, where a small amount of known calibration gas was added to the inlet stream. The standard additions were used to validate corrections made to the gas substitution calibrations to account for the lack of water vapor in the calibration. The standard additions were alternated with the gas substitution calibrations. Based on the calibrations conducted during the study, the NO_y conversion efficiency was constant over the course of the study at approximately 90-95%. Uncertainty for the NO_y measurement is estimated at ±25% for accuracy and ±25% for precision.

2.4.4. Aeronomy Laboratory (NOAA1; NOAA2). NO_y was converted to NO with a tube of pure Au (0.6 cm OD X 30 cm) heated to 300°C in the presence of either CO or H₂. The resulting NO was measured with a custom-built NO-O₃ chemiluminescence instrument. The inlet system for

this instrument is shown in Figure 5. Two Au tube converters were connected to the same chemiluminescence instrument via valves. Each converter was a stand-alone unit with separate calibration gas inlets, CO or H₂ gas inlets, and heating controls. The flow of pure reductant gas was 0.3% of the total flow (1 slpm) through each channel. One channel (NOAA2) used CO throughout the study. The other channel (NOAA1) initially used CO but about midway through the study was switched to H₂ to evaluate under field conditions the NO_y conversion efficiency of this less toxic gas. With H₂ the background levels were lower by about 10% and the conversion of NH₃ was higher by about 8%. No other differences were found. The lower background level with H₂ over CO may be due to chemiluminescence of metal carbonyl species in CO or might be due to increased H₂O exiting the converter, as reported by *Kliner et al.* [1997]. The principal calibration gas used was NO₂ that was derived from gas-phase titration of the primary NO standard (Scott-Marrin, Inc.) with O₃ produced via a Hg penray lamp. The converters were normally maintained at a temperature of 300°C.

Conversion efficiency was checked periodically with NO₂. However, since NO₂ is relatively easily converted to NO the converters were also evaluated with HNO₃ and NPN. These tests were generally performed in zero air due to the large and

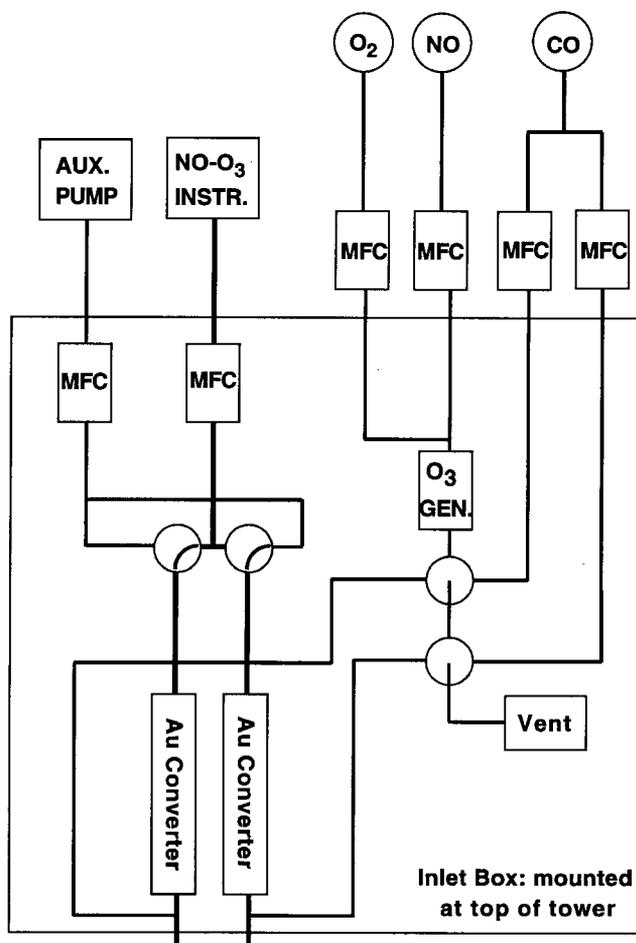


Figure 5. Schematic diagram of the NOAA NO_y inlet. The O₃ generator houses a Hg penray lamp that produces sufficient O₃ to almost completely titrate the NO calibration gas to NO₂. Simultaneously switched three-way valves route the sample flow (heavy line) from either Au converter to the chemiluminescence instrument via a mass flow controller (MFC).

variable ambient NO_y levels. Conversion efficiency was determined by the ratio of the NO_y signal with the converter at 300°C to that obtained with the converter at 550°C. Tests for conversion of NH₃ in zero air were also performed. When any of these tests indicated that a converter was not operating correctly, that tube was heated to 550°C for 1-2 hours. This procedure usually was sufficient to restore near-unity (>95%) conversion. On two occasions during the study the Au tube designated NOAA2 required more rigorous cleaning. This was accomplished with a 6 M HCl wash using a stiff bristled brush followed by numerous washes with distilled deionized water. The cleanliness of the converters was periodically evaluated by measurement of NO_y in zero air, which was assumed to contain little or no NO_y. These so-called artifact levels were always small (-2 to 30 pptv) and were neglected.

Photon counting was used to acquire the signal from the photomultiplier tube. Instrument sensitivity was determined every 5 hours with 8 min periods of NO₂ standard additions for each converter. Instrument background levels were determined every 5 hours over 8 min periods. NO_y mixing ratios were calculated by subtraction of the background signal from the ambient NO_y signal level and dividing by the sensitivity. For this calculation, linear interpolation between averaged sensitivity determinations and between averaged background measurements was performed. This procedure was necessary because the instrument performance can vary with environmental changes. For example, changes in atmospheric water vapor levels can directly affect the instrument sensitivity because water is an efficient quenching agent of the electronically excited NO₂ molecule that produces the chemiluminescence [Kley and McFarland, 1980]. The sensitivity values did show variability (RSD = 7%), but this was also due to the difficulty in determining the sensitivity with rapid changes in ambient NO_y during calibration periods. No attempt was made to isolate variations due to environmental factors from those due to data reduction. The result was an increase in uncertainty of the NO_y data.

The average instrument NO sensitivity was 1.9 Hz pptv⁻¹, and the average background level was 290 Hz. Thus for 1 s integration and S/N=2 this instrument had a detection limit of less than 20 pptv (as NO). Precision was estimated from the RSD of a series of NO_y measurements during periods of constant atmospheric conditions (i.e., constant mixing ratios). Four such periods were examined for each of the separate gold tubes, and the maximum RSD level found was ±3%. Accuracy is more difficult to assess for this measurement. If the NO_y converter is operating optimally (i.e., near-100% conversion of all NO_y species to NO with no losses, artifacts, or interferences), then the accuracy for NO_y is similar to that for the determination of NO. In that case, the inaccuracy due to uncertainties in (1) mass flow controllers, (2) the primary NO standard, and (3) the variability of the background and sensitivity levels, via propagation of errors calculation, is calculated to be ±9%. However, there is uncertainty in the conversion efficiency for the different NO_y (and non-NO_y) species as well as potential losses in the inlet, all of which we estimate to contribute ±15%. Thus the total estimated RMS uncertainty for the NOAA NO_y data is ±18%.

2.4.5. Tennessee Valley Authority (TVAG; TVAM). Two separate instruments measured NO_y via the conversion of NO_y to NO with heated metal catalysts. The resultant NO was measured via NO-O₃ chemiluminescence in separate TEII 42S NO-NO_x analyzers that were operated on the

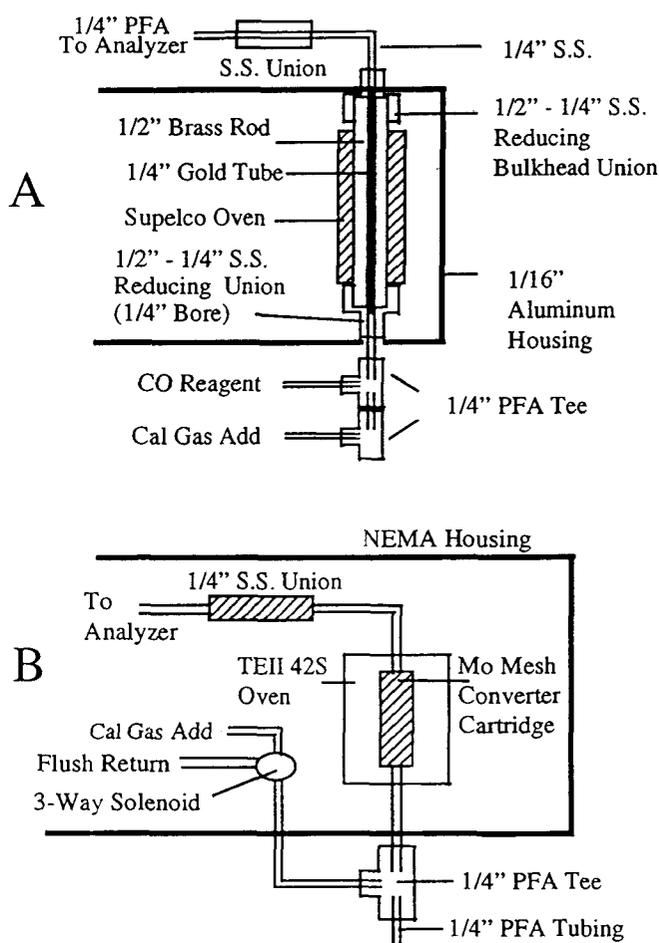


Figure 6. (a) Schematic diagram of the TVAG NO_y inlet. (b) Schematic diagram of the TVAM NO_y inlet.

100 ppbv range. The configuration of one system (TVAG) is shown in Figure 6a. A 0.6 cm OD Au tube was placed inside a 1.2 cm OD brass rod which was drilled just large enough to allow insertion of the Au tube. The brass rod was positioned inside a heating oven which was placed inside an aluminum housing. The temperature of the oven was controlled at 320°C. A 6.4 cm by 0.6 cm OD PFA Teflon tube connected the sample inlet line to the Au tube via a stainless steel reducing fitting which was bored out to allow the Teflon line to be butted against the Au tube. The sample inlet line consisted of two PFA Teflon tees connected to each other via 0.6 cm OD PFA Teflon tubing. The outside tee was for calibration gas addition to the sample line while the inner tee was used to add CO at about 30 sccm. The total length of the sample inlet line was about 10 cm. The second system (TVAM) configuration is shown in Figure 6b. The MoO mesh converter and oven assembly was removed from a TEII 42S and placed into a weatherproof (NEMA) housing. The thermocouple and power cables were extended to allow the 42S analyzer to control the oven temperature at 340°C. The calibration gas addition was conducted through a PFA 0.6 cm tee that connected the converter cartridge tubing to a ~5 cm long Teflon tube to extend beyond the NEMA housing.

Both systems were calibrated using NO calibration gas obtained from Scott Specialty Gases (EPA Protocol gas; Plumsteadville, Pennsylvania), and diluted with processed

ambient air produced from a TEII Model III clean air system. This clean air was also used to determine the instrument background levels. Both NO_y systems were calibrated with the NO calibration gas in a synthetic clean air matrix to check for linearity at the lower measurement levels. The converter efficiencies for both systems were checked using NO₂ produced from the gas-phase titration of NO with O₃ within a TEII Model 146 gas calibration system.

The data reduction process first involved the subtraction of the system zero reading which was obtained from the average of the clean air additions to the sample inlet lines. The system sensitivities, which were measured every 12 hours using NO calibration gas, were also averaged over the entire study period (providing no significant change was evident) and applied to their respective measurement systems. The system sensitivities were determined via the addition of the standard NO calibration gas to the ambient air sample. Since the signal difference depends on the subtraction of the ambient air signal, the system sensitivities determined during periods of rapidly changing NO_y levels were eliminated from the averaging calculations. The fluctuations in the remaining system sensitivity determinations are partially due to the changing ambient NO_y levels during the gas addition periods and also due to changing sample line matrix effects. For these analyzers under the field conditions described here the NO detection limit is estimated to be 0.3 ppbv for 1 min samples. Precision and accuracy are controlled by the efficiency of the converter to convert all NO_y species to NO with no losses or artifacts and the uncertainty of line losses under different atmospheric conditions. The precision is influenced principally by the sensitivity fluctuations and is estimated to be $\pm 20\%$; accuracy is estimated to be $\pm 30\%$. Finally, we note here that the TVA data have been revised since they were first submitted. After the first round of analyses several of the plots comparing the NO_y data indicated a probable error in the data reduction routine. The error was found and the data were resubmitted after revision.

2.5. Additional Measurements

Separate NO_y species measurements were conducted by the NOAA group. NO and NO₂ were measured by chemiluminescence and photolysis/chemiluminescence with total uncertainties estimated at $\pm(19\% + 17 \text{ pptv})$ and $\pm(22\% + 28 \text{ pptv})$, respectively [Williams *et al.*, 1997]. Peroxyacyl nitric anhydrides (PAN, peroxypropionyl nitric anhydride, PPN, and peroxyacetic nitric anhydride, MPAN) were determined via gas chromatography with total uncertainties estimated at $\pm 21\%$ for PAN and $\pm 30\%$ for PPN and MPAN [Williams *et al.*, 1997]. HNO₃, particulate NO₃⁻, and particulate NH₄⁺ and SO₄²⁻ were determined with Teflon/Nylon filter pack sampling and ion chromatography analysis. Total method uncertainties for these species are estimated at $\pm 21\%$ [Williams *et al.*, 1997]. NH₃ was measured via citric acid denuder/ion chromatography and O₃, CO, and SO₂, were measured with commercial instruments. Surface meteorological data (9 m) were taken, and data on boundary layer winds were collected with a 915 MHz radar profiler. Daily samples of ambient air at this site were taken with stainless steel canisters and analyzed for non-methane hydrocarbons by gas chromatography by a research group from the University of Miami.

2.6. Measurement Protocols

Two protocols were implemented for this study: ambient air sampling and spiking tests. Ambient air was sampled

continuously from the normal instrument inlet systems with the inlets located as close together as possible and at a common sampling height (9 m above ground). This was deemed most likely to reflect the actual sampling conditions encountered in field measurements and give the most realistic assessment of the differences, if any, among the instruments and their associated inlets.

The NO_y instruments also were periodically challenged with samples provided from sources of NO (gas cylinder), NO₂ (titrated NO from gas cylinder), HNO₃ (permeation tube in self-contained temperature, pressure, and flow controlled source), NPN (gas cylinder), and NH₃ (gas cylinder). The NO, NO₂, and NPN sources were calibrated by the NOAA NO_x and NO_y instruments (the NPN was determined with an Au converter at 550°C in zero air), and the HNO₃ and NH₃ sources were calibrated by bubbling the gas through water-filled impingers followed by analysis of the solution with an ion chromatograph. The spike test samples were introduced directly into the instrument inlets via separate 0.3 cm OD PFA Teflon tubes as low flow (10 sccm) standard additions to the ambient air sample. Large and changing background concentrations were a common occurrence during the study and introduced imprecision into the tests. Also, the BNL and ESE sample inlet flows were larger ($\sim X3$) than the other inlet flows which meant that the actual levels delivered to those systems during the spike tests were lower by the same factor. By necessity, then, the spike tests were administered during periods when the NO_y mixing ratios appeared to be stable and at lower levels. This complicates the generalization of instrument performance at high NO_y levels from the spike tests.

3. Results

During the early part of the study the NOAA group evaluated the separate low ppmv NO in N₂ gas standards that the participants used to determine NO_y levels. The results indicated that the two NOAA tanks were about 3.5% lower in NO mixing ratio relative to the other four. Since the differences were small, no corrections were made to the data.

3.1. Overall Comparisons

Table 1 provides an overview of the total 1-min averaged data sets provided by each investigator. The great number of data points combined with a large degree of overlap during sampling provided the opportunity to use only coincident data points for this analysis. A summary of this reduced data set of 1174 common 1-min data is shown in Table 2. Since the NOAA1 and NOAA2 gold tubes were connected to the same

Table 1. Summary of All NO_y Data

Laboratory	Total Points	Data Period
BNL	25613	June 16 to July 15
ESE	29562	June 21 to July 15
GIT	6641	July 1 to July 16
NOAA1	14958	June 22 to July 19
NOAA2	14329	June 22 to July 19
TVAG	23275	June 25 to July 15
TVAM	27202	June 23 to July 15

Table 2. Statistical Summary of All Coincident NO_y Data

Laboratory	Mean	s.d.	Minimum	Maximum
BNL	12.67	8.92	2.45	82.59
ESE	11.88	8.68	2.39	78.70
GIT	8.59	6.95	1.17	60.87
NOAA1*	10.90	8.53	1.89	80.98
NOAA2	11.46	9.45	2.34	89.34
TVAG	11.02	8.21	2.24	77.79
TVAM	11.31	7.76	1.85	72.04

Data are in ppbv. Number of points equal to 1174.

*NOAA1 data were linearly interpolated to NOAA2 timebase.

chemiluminescence instrument, the two converters could not be sampled simultaneously. Thus the NOAA1 data were linearly interpolated over the same times as the other data which resulted in slightly greater scatter. With the exception of the GIT data, these data sets are clearly similar to one another. For example, the RSD of the mean values is less than 6% (11% when the GIT data are included). Figure 7 shows scatterplots of these data (and the one-to-one line) with ESE arbitrarily chosen as a common basis of comparison. There is tight correlation about the one-to-one line in many of these plots; linear least squares analyses of these data sets are described below. The crosses in Figures 7c and 7d are twelve 1-

min averages of NOAA1 and NOAA2 data that are clearly outliers with respect to the other 5 data sets. It is not known why these points were low for this short interval. Although these points are shown here for completeness, they have been excluded from further analyses.

Linear least squares fitting was done to these data using a weighted regression routine; thus the slope calculated for one x-y pair of data sets is the inverse of the slope for the same pair but with the axes inverted (i.e., the y-x pair), and the intercepts are approximately the negative of each other. (This is not true of standard unweighted linear regression routines.) The weighting factors were the inverses of the total

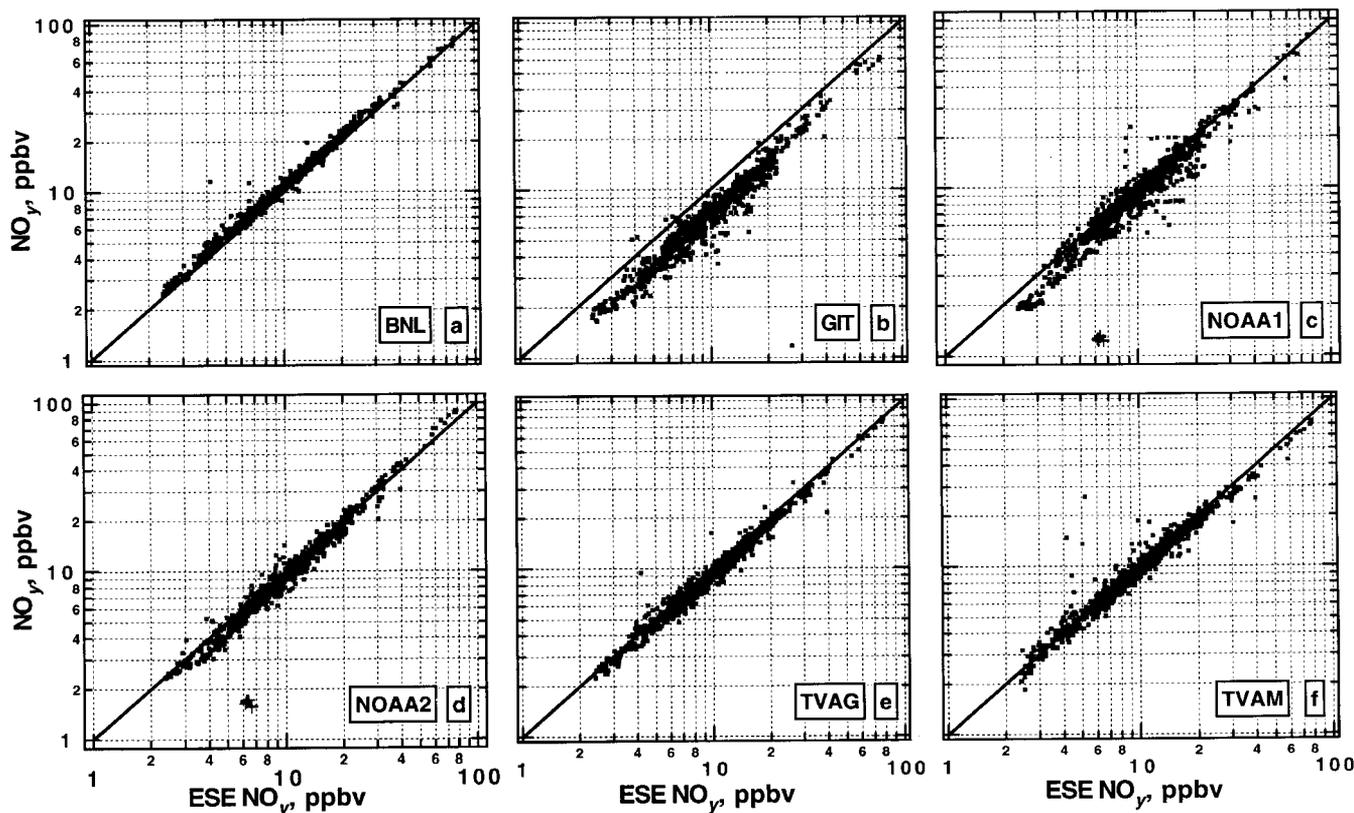


Figure 7. Scatterplots of NO_y data from different groups versus the ESE NO_y data. The line is that of one-to-one correspondence. The crosses shown in Figures 7c and 7d are apparent outliers in the NOAA data that are shown on the plots but not included in the analyses. (a) BNL NO_y, (b) GIT NO_y, (c) NOAA1 NO_y, (d) NOAA2 NO_y, (e) TVAG NO_y, (f) TVAM NO_y.

Table 3. Weighted Linear Least Squares Fitting Coefficients for Combinations of NO_y Data

	BNL	ESE	GIT	NOAA1	NOAA2	TVAG
ESE	0.93±0.02 0.01±0.13					
GIT	0.66±0.01 -0.16±0.11	0.73±0.02 -0.18±0.14				
NOAA1	0.88±0.01 -0.42±0.08	0.98±0.02 -0.57±0.13	1.35±0.03 -0.34±0.15			
NOAA2	0.91±0.01 -0.30±0.08	0.98±0.02 -0.31±0.14	1.36±0.03 0.11±0.16	1.01±0.02 0.23±0.09		
TVAG	0.84±0.02 0.11±0.15	0.91±0.02 0.11±0.18	1.24±0.04 0.36±0.19	0.91±0.02 0.71±0.15	0.93±0.02 0.41±0.15	
TVAM	0.86±0.02 0.23±0.15	0.93±0.03 0.25±0.18	1.27±0.04 0.50±0.19	0.94±0.02 0.82±0.15	0.94±0.02 0.55±0.15	1.02±0.03 0.14±0.21

Number of points equal to 1174. For the fit, the "x" coordinate data are those shown across the top of the table. The upper value in each cell is the slope, and the lower value is the intercept in ppbv. Uncertainties are standard errors.

uncertainty of each data point. The resulting linear least squares fitting coefficients (slopes and intercepts and uncertainties of the fitted lines) are shown in Table 3. The squared correlation coefficient for any combination of data sets is 0.9 or greater. The column of data labeled ESE in this table correspond to the plots in Figure 7. Most of the slopes are in the range 0.85 to 0.95, except for comparisons with the GIT data for which the slopes are in the range 0.65 to 0.78. Thus while the majority of the data show good overall consistency, there appears to be a systematic difference between the GIT data and the rest of the data sets. The intercepts span the range from -0.57 to 0.82 ppbv with the majority in the range ±0.35 ppbv.

3.2. Spike Tests

These tests (also called challenges) were additions of individual calibrated standards directly into the NO_y inlets while the instruments were measuring ambient air. Four NO_y species and one non-NO_y compound were tested. The results of these tests are reported as fraction of compound converted. Spike tests were administered sequentially to the inlets of each instrument, and the levels of the spike gases were of the same magnitude as the ambient NO_y levels. Each round of challenges could take as much as 2 hours and during this time the ambient NO_y could change significantly. The consequence was that the precision of the tests could be good (if ambient NO_y was stable and low) or poor (variable and high ambient NO_y). Because of higher inlet sample flow rates, some instruments (BNL and ESE) experienced greater dilution of the spike sample which made the spike tests somewhat more difficult than for those instruments with lower sample flows. Figure 8 and Table 4 show the results from the spike tests. In Figure 8 the tests are segregated by compound (Figures 8a-8d)

and by date, shown on the abscissas. The symbols are results from individual tests, and the dashed line shows unit conversion.

3.2.1. NO_x spike tests. Figure 8a shows the results from the two tests with NO as the spike gas. While this is not a test of NO_y conversion, it does provide an indication of the level of precision possible given the conditions at this site. Data from the test on July 29 clustered around the unit conversion line, but data from the second test showed more scatter. This was attributed to changing background levels.

Results from four tests of NO₂ conversion are shown in Figure 8b. The data tended to cluster around the unit conversion line and exhibited a similar level of scatter to that seen in the NO tests. Since NO₂ is not a difficult compound for the NO_y catalysts to convert, results from these two compounds (NO and NO₂) indicate the maximum level of agreement to be expected from spike tests administered during this experiment. Only a few data points were outside of ±10% from unity, and only two were outside of ±20%. Thus there did not appear to be any systematic problems associated with any of the instruments when NO_x was tested.

3.2.2. NPN spike tests. Results from these tests are shown in Figure 8c. Considerably more data scatter is apparent for these tests than for NO or NO₂. The BNL data fell mostly within ±10% of unit conversion, with the exception of one outlying point on July 4. The ESE data fell mostly within ±20% of unit conversion, but had a tendency toward greater levels of NPN measured than those added. Both NOAA converters had 50-70% initial conversion, but exhibited increasingly higher conversion efficiency over time, up to 90%. Only one data point was available from the GIT instrument which showed 75% conversion. Both TVAG and TVAM data indicated excellent recovery, although the TVAM data had somewhat more scatter than TVAG.

Table 4. Statistical Summary of All Spike Tests

Laboratory	HNO ₃	NPN	NO ₂	NO	NH ₃
BNL	0.65±0.13 (5)	1.04±0.19 (6)	1.10±0.11 (4)	1.04±0.09 (2)	0.00±0.00 (2)
ESE	1.14±0.27 (7)	1.07±0.18 (6)	1.02±0.12 (4)	0.88±0.34 (2)	0.05±0.03 (2)
GIT	0.73±0.15 (2)	0.74 (1)	0.86 (1)	0.84 (1)	N/A
NOAA1	0.59±0.07 (4)	0.76±0.12 (4)	0.89±0.05 (4)	0.99±0.02 (2)	0.10±0.03 (2)
NOAA2	0.52±0.06 (4)	0.75±0.17 (4)	0.97±0.05 (2)	0.79 (1)	0.02±0.03 (2)
TVAG	0.83±0.11 (4)	1.00±0.02 (3)	0.97±0.01 (2)	1.00±0.09 (2)	0.00±0.00 (2)
TVAM	0.93±0.05 (4)	1.03±0.13 (4)	1.02±0.07 (2)	1.02±0.11 (2)	0.08±0.00 (2)

Data are fraction of compound converted: mean ±1 standard deviation (number of points). N/A indicates that no data are available for that test.

3.2.3. HNO₃ spike tests. Results from these tests are shown in Figure 8d. The BNL data were all in the 50–75% conversion range. The ESE data varied from 80 to 165% conversion with an apparent bias of recovered HNO₃ greater than that added, also seen in the NPN data. The NOAA data had

little scatter but were consistently lower than the added HNO₃ with conversion efficiencies between 40 and 65%. The two points from the GIT instrument also showed somewhat low conversion (65 and 85%). The TVAM system had little scatter and very good conversion for HNO₃ (85 to 100%) while

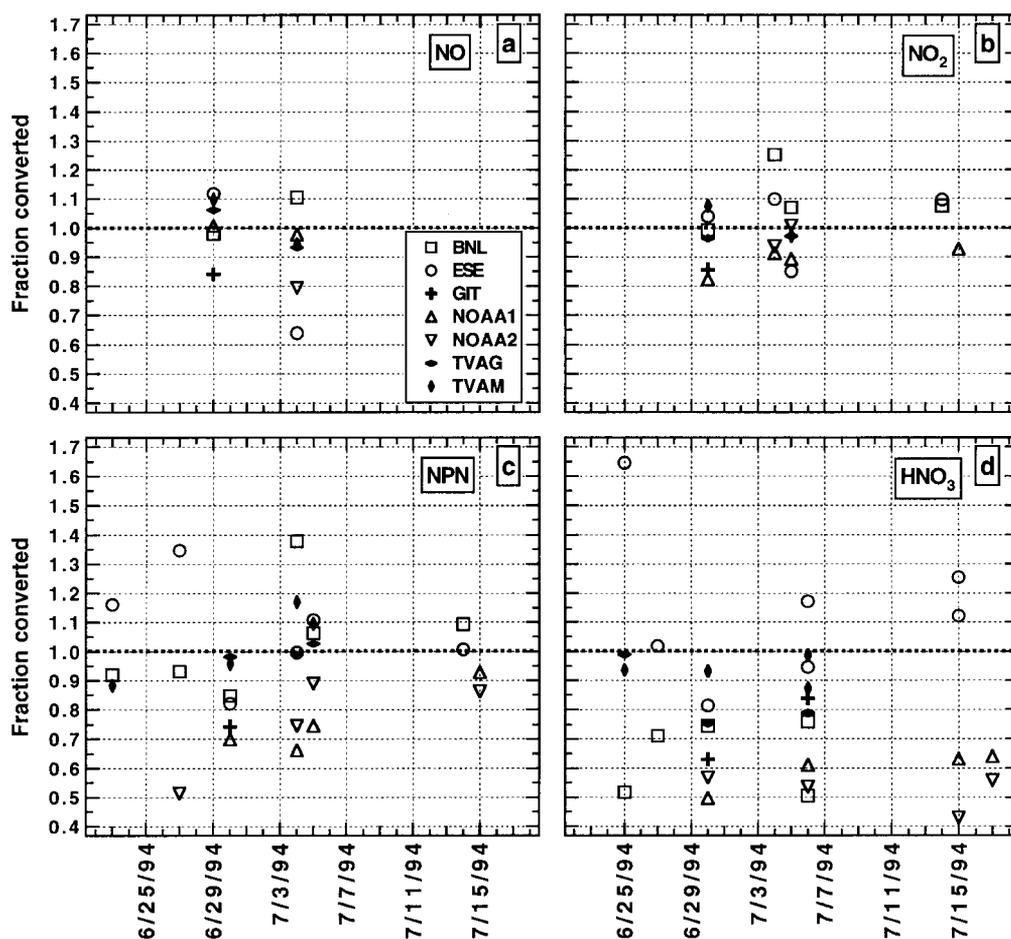


Figure 8. (a) Results from the NO spike tests in fraction converted. The symbols represent single spike test results from the groups shown in the legend. The dashed line is the mixing ratio of NO in the tank used to provide the spike. (b) Results from the NO₂ spike tests in fraction converted. (c) Results from the NPN spike tests in fraction converted. (d) Results from the HNO₃ spike tests in fraction converted.

conversion for the TVAG system was slightly lower (75 to 100%) .

3.2.4. NH₃ spike tests. Conversion of this compound was tested by addition of a known large level (35–114 ppbv) of NH₃ into the inlets in a manner similar to the other tests, although not all of the instruments were involved in this test. These results are also given in fraction converted, which was calculated by dividing the level of NO recovered by the level of NH₃ added (see Table 4). Three Mo converters and three Au converters were evaluated in the first test on July 10. The lowest recovery was reported by the BNL and TVAG instruments which essentially had no response to added NH₃. The other two Mo converters tested (ESE and TVAM) both showed conversion at the 5–8% level. The NOAA1 and NOAA2 Au converters had conversion efficiencies of 12 and 4%, respectively. However, these tests were conducted at converter temperatures of 500°C which is higher than the normal temperature of 300°C. When the tests were redone on July 11 at the lower temperature, the conversions were 8 and 0%, respectively. The consistently higher conversion for NOAA1 may be due to the use of H₂ for reductant gas as opposed to the normally used CO; however, this was not conclusively shown and further testing is planned. Ambient levels of NH₃ were measured during a portion of the experiment and ranged from 0.1–1.2 ppbv, thus it was not a significant interference to the NO_y measurements at this site.

3.2.5. Spike test summary. A summary of all of the spike tests by group and by compound is presented in Table 4. The results are shown as fraction of compound converted and are given as the mean, one standard deviation, and the number of tests for that instrument/species combination. On average, the BNL instrument had good conversion efficiency for all of the NO_y species except HNO₃ and had no conversion of NH₃. The ESE system also exhibited good overall conversion, but with greater scatter, and had modest conversion of NH₃. The GIT data were consistently low in conversion for the more oxidized NO_y compounds. The two NOAA converters exhibited similar conversion efficiencies for all of the tested NO_y compounds except NO, but they had low conversion for the more oxidized NO_y compounds (NPN and HNO₃). NOAA1 converted NH₃ but NOAA2 did not at 300°C. The two TVA instruments exhibited the most consistent and quantitative recoveries of all of the spike compounds tested. The TVAM system had a modest degree of NH₃ conversion, but TVAG showed no conversion.

4. Discussion

The NO_y data sets will be discussed with respect to (1) how they compare on an overall basis, (2) how well the converters operated during a specific episode with varying NO_y composition, (3) the comparison of spike data to that found from ambient measurements and (4) whether differences are evident between Au and Mo converters.

4.1. Normalized Difference Comparisons

The scatterplots shown in Figure 7 and the weighted least squares slopes and intercepts shown in Table 3 indicate that with the exceptions of the GIT and NOAA1 data, there are only small differences among the NO_y data sets. In order to examine these differences in more detail, we define a quantity called the normalized difference (ND) which is the difference between a particular measured NO_y data point and the average NO_y at that

time divided by the average. Five of the NO_y data sets were used to define the average: BNL, ESE, NOAA2, TVAG, and TVAM. The GIT data were excluded because of the obvious systematic difference, and the NOAA1 data were excluded because those data were interpolated. For these calculations, the same 1174 point data sets that are summarized in Table 2 are used.

4.1.1. Normalized difference histograms.

These plots, shown in Figure 9, are frequency histograms that were binned in 5% intervals and plotted such that the integral under all of the bars corresponds to all of the data. The offset of the centroid of a distribution from the line of zero difference (solid line) is a measure of the overall level of difference of a data set from the average NO_y. Thus the GIT data are 25–30% lower overall than the average (Figure 9c). Qualitatively, the shapes of the histograms indicate both how tightly clustered a data set is and whether differences are more likely to be greater or less than the mean difference. For example, the histogram in Figure 9d shows skewness to differences smaller than the

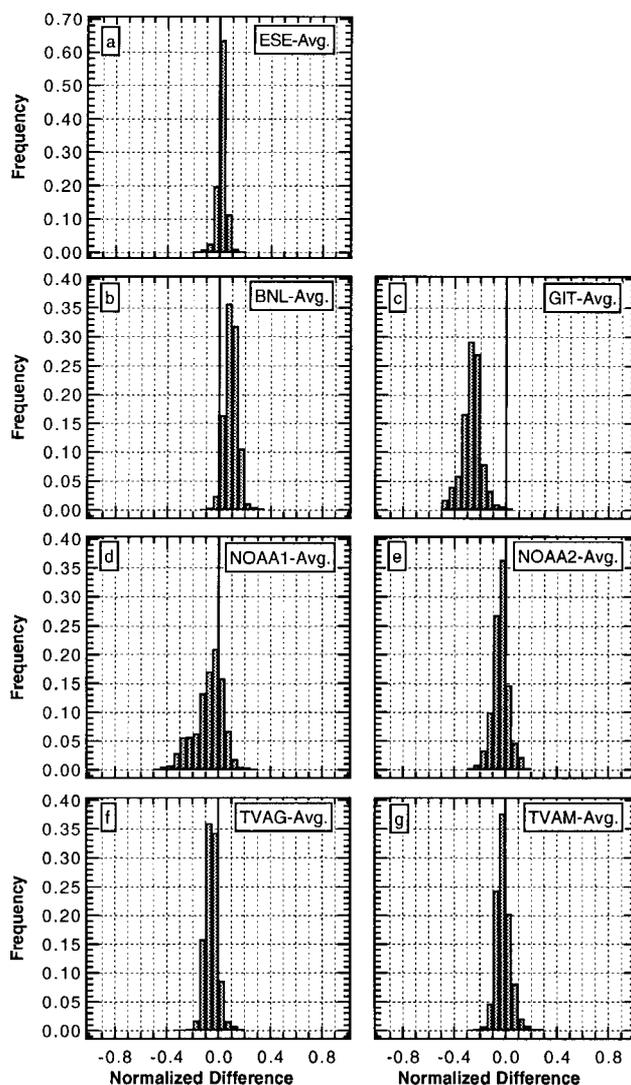


Figure 9. Normalized difference histograms of individual NO_y data minus average NO_y data. The average NO_y data were calculated from the BNL, ESE, NOAA2, TVAG, and TVAM data sets. Only coincident 1 min averages of NO_y were used (N=1174). (a) ESE NO_y, (b) BNL NO_y, (c) GIT NO_y, (d) NOAA1 NO_y, (e) NOAA2 NO_y, (f) TVAG NO_y, (g) TVAM NO_y.

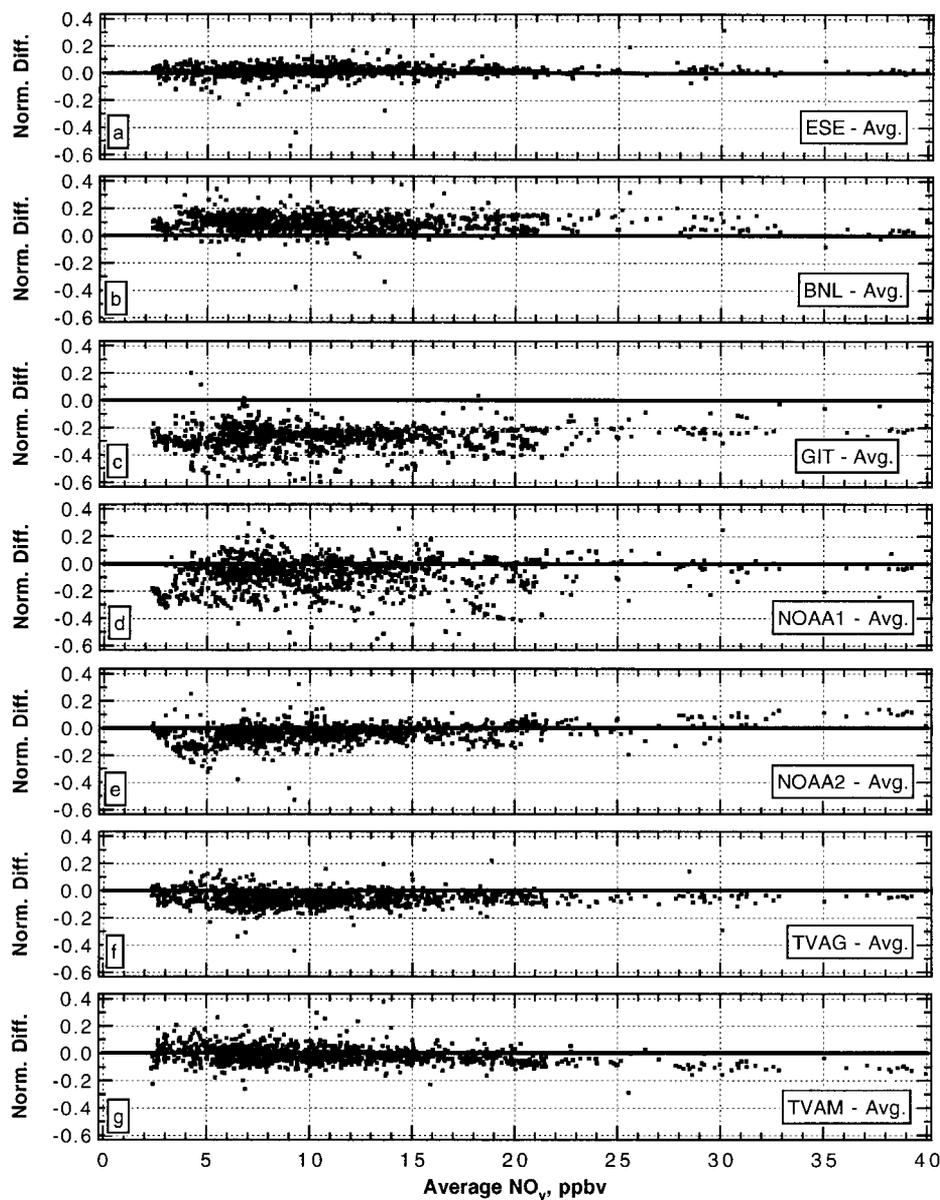


Figure 10. Normalized difference NO_y data versus average NO_y data. (a) ESE NO_y, (b) BNL NO_y, (c) GIT NO_y, (d) NOAA1 NO_y, (e) NOAA2 NO_y, (f) TVAG NO_y, (g) TVAM NO_y.

mean, which indicates that NOAA1 was more likely to underestimate NO_y, with respect to average NO_y, than to overestimate.

The data distributions show that the best agreement of average NO_y is with ESE (Figure 9a; note different *y* scale than with Figures 9b-9g). The ND data are tightly clustered with over 80% of the data no more than $\pm 5\%$ away from the point of zero difference. The BNL data (Figure 9b) are also tightly clustered, but are higher than the average by 5-10%. The GIT data (Figure 9c) exhibit a significant negative offset from the average NO_y and are not as peaked as the ESE or BNL data. The offset no doubt arises from a systematic error. The principal investigator from the GIT group has indicated that the system used to calibrate the TEII 42s instrument did not operate correctly while the measurements were underway. The NOAA1 data (Figure 9d) are offset from the average data by 5-10%, although some of this offset ($\sim 3\%$) is due to a difference in calibration standards. There is, however, a large spread in the

ND values from NOAA1 with a skewness toward lower NOAA1 NO_y. One source of some of this scatter is the linear interpolation of the NOAA1 data to the timebase common for the data shown in this analysis. The NOAA2 data (Figure 9e) are offset from the average by 5-10% which is similar to the NOAA1 data. However, the NOAA2 data show a tighter cluster than NOAA1 with an equal tendency to be higher or lower than the average data. The overall agreement of average NO_y with TVAG (Figure 9f) or with TVAM (Figure 9g) is similar at the 0-5% level. However, the TVAG distribution is more tightly clustered than is the TVAM distribution.

4.1.2. Normalized difference versus NO_y. Figure 10 shows the different ND data sets plotted as a function of the average NO_y. Features seen in the histogram plots, such as the 25-30% offset in the GIT data and the scatter in the NOAA1 data, are also visible in these plots. However, none of these data sets exhibits any significant trend (i.e., slope) with respect to average NO_y. The increased scatter in the GIT and

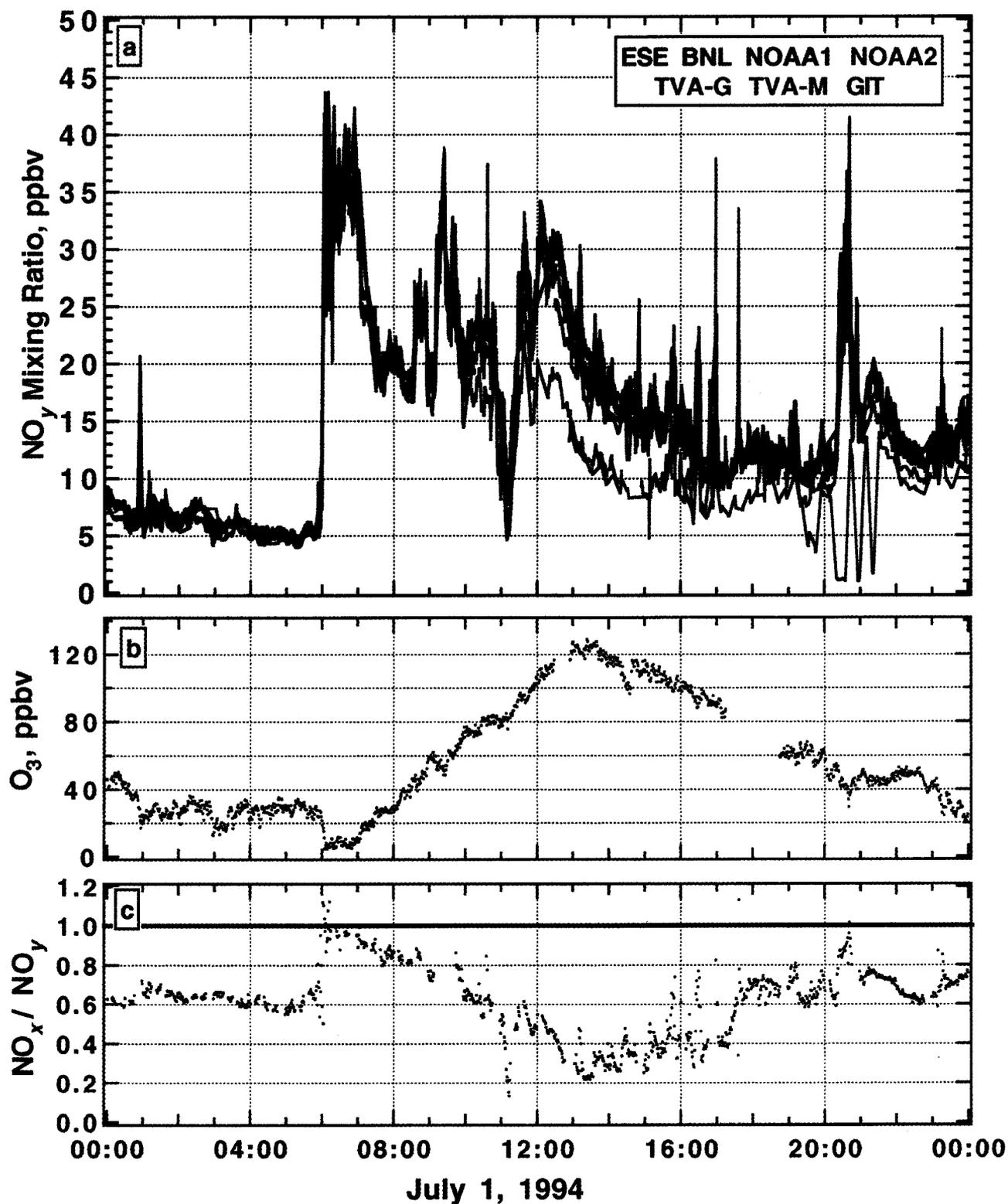


Plate 1. (a) NO_y data for July 1, 1994. (b) O_3 data (NOAA) for July 1, 1994. (c) NO_x/NO_y data (BNL) for July 1, 1994.

NOAA1 data occurs in the 5-15 ppbv NO_y region and appears to be biased to an underestimate of NO_y with respect to the average.

This more detailed analysis of the overall common NO_y data indicates that five of the seven measurements agreed very well

over a wide range of NO_y mixing ratios. However, two of the seven measurements had problems. The GIT data showed a sizable systematic negative difference with respect to average NO_y and a tendency more to underestimate than overestimate NO_y mixing ratios. The NOAA1 data also had a tendency to

underestimate NO_y levels. These problems are related to the photochemical conversion of NO_x into more oxidized NO_y species, which is discussed next.

4.2. NO_y Measurement Differences Due to Photochemistry

The 24-hour period covering July 1-2 was perhaps the most interesting episode of the entire study. The NO_y data, O₃, and NO_x/NO_y are shown in Plate 1. The level of NO_y was less than 10 ppbv until 0600 LT (local time refers here to Eastern Standard time) when it increased from about 5 ppbv to over 30 ppbv in less than 10 minutes. The increase in the ratio of NO_x to NO_y and the sharp decrease in O₃ at 0600 indicated the incursion of a large amount of NO_x. Then during the late morning and early afternoon hours, O₃ increased steadily from 5-10 ppbv and peaked at about 125 ppbv; this correlated with a steadily declining NO_x to NO_y ratio. In the early afternoon the ratio was approximately 0.3, which indicated substantial photochemical conversion of NO_x to more highly oxidized nitrogen oxides. After the O₃ peak at 1300-1400, NO_x/NO_y increased and eventually levelled off at 0.7.

The NO_y data revealed interesting and sometimes substantial differences among the instruments over this period. Prior to the large increase at 0600 when NO_x/NO_y was

0.6-0.7 some small differences were apparent. For example, NOAA1 and NOAA2 were 15-20% lower and TVAG was ~20% higher than the BNL, ESE, and TVAM data. After the large increase when NO_x/NO_y approached unity, the NO_y data from all of the instruments converged. As photochemistry then reduced NO_x/NO_y, the NOAA1 NO_y data separated from the rest and was lower by 50% or more at the time of peak O₃. The same was true of the GIT system. Later in the day when NO_x/NO_y increased to ~0.7 (around 2100 LT) the data converged again, except that from the GIT system.

Examination of the traces of the individual NO_y species for this period supports the view that the GIT and NOAA1 converters were not measuring all of the NO_y. Figure 11a shows the NO_x, PAN, HNO₃, and NO₃⁻ mixing ratios and Figure 11b shows the ratios of these species to NO_y measured by the NOAA2 instrument. Table 5 shows the mixing ratios of all of the NO_y and NO_y species data integrated over the sampling times of the HNO₃ measurements (see Figure 11a), where data gaps have been linearly interpolated. By the time the peak O₃ value occurred at 1300 the ratio HNO₃/NO_y was about 0.20. Qualitatively, this event correlated well with the separation of the NOAA1 and GIT NO_y measurements from the other five, for which excellent agreement was found - RSD values are 3-11%. For a more quantitative analysis, the GIT data were artificially increased by 25% and the NOAA1 data were artificially

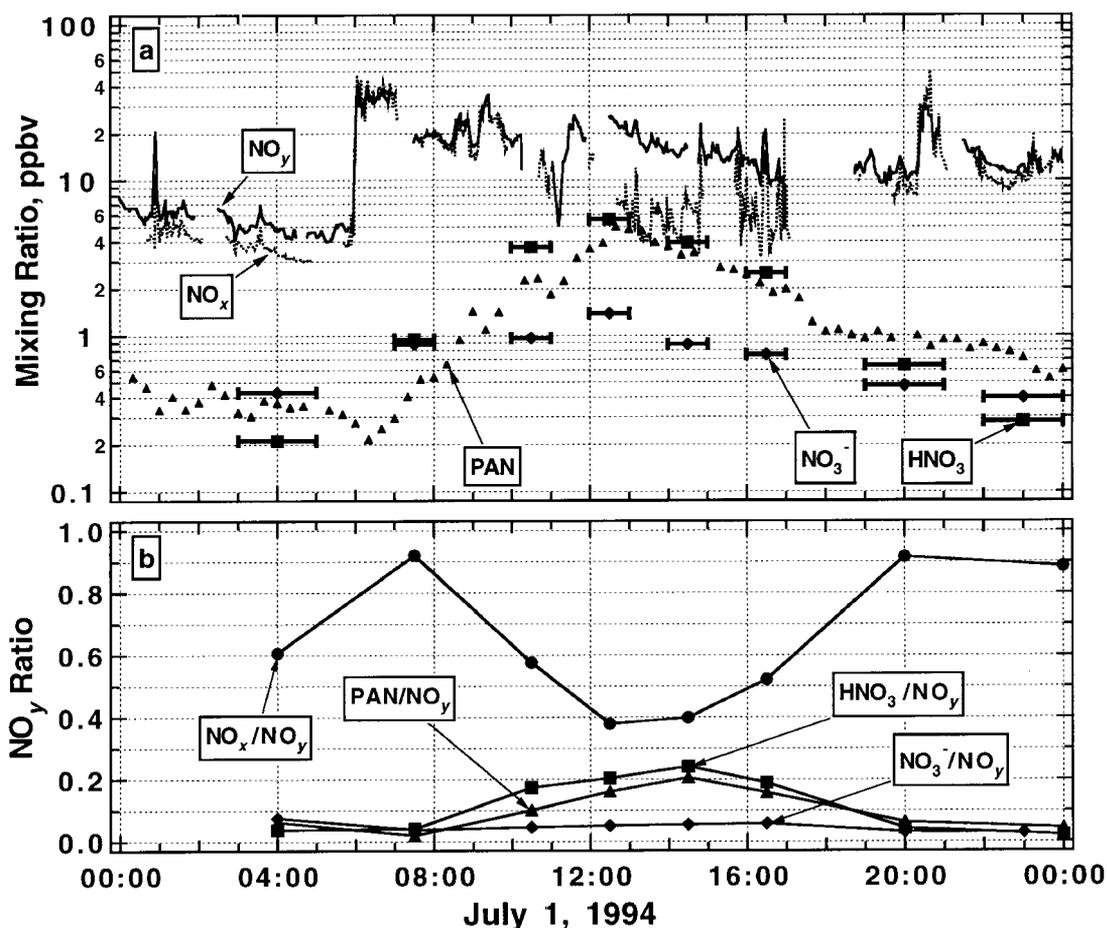


Figure 11. (a) NO_y and NO_y species data (NOAA) for July 1, 1994. The horizontal bars show the sampling period for the HNO₃ and NO₃⁻ data. (b) Ratios of individual NO_y compounds to measured NO_y for July 1, 1994. For each point the data were averaged over the sampling time of the HNO₃ measurements (horizontal bars in Figure 11a). Lines between the points are shown to help illustrate trends.

Table 5. NO_y Species and NO_y Averaged Over Selected Periods on July 1, 1994.

Species	03-05	07-08	10-11	12-13	14-15	16-17	19-21	23-01
NO _x	3.46±0.79	22.0±3.7	12.2±2.4	10.4±2.1	6.55±1.37	6.96±1.46	14.2±3.2	12.2±2.7
HNO ₃	0.21±0.04	0.94±0.20	3.69±0.78	5.59±1.17	3.94±0.83	2.52±0.53	0.64±0.13	0.28±0.06
NO ₃ ⁻	0.43±0.09	0.88±0.18	0.96±0.20	1.38±0.29	0.88±0.19	0.75±0.16	0.47±0.10	0.40±0.08
PAN	0.35±0.07	0.45±0.09	2.14±0.45	4.37±0.92	3.36±0.71	2.10±0.44	0.97±0.20	0.59±0.12
PPN	0.05±0.02	0.09±0.03	0.38±0.11	0.80±0.24	0.47±0.14	0.25±0.08	0.12±0.04	0.09±0.03
MPAN	0.02±0.00	0.02±0.01	0.15±0.05	0.14±0.04	0.07±0.02	0.04±0.01	0.04±0.01	0.03±0.01
Sum NO _y [*]	4.52±0.80	24.0±3.7	19.6±2.6	23.5±2.6	15.3±1.8	12.6±1.6	16.5±3.2	13.6±2.7
BNL	5.68±0.57	21.6±2.2	19.4±1.9	27.5±2.8	16.5±1.7	14.4±1.4	16.3±1.6	14.7±1.5
ESE	5.70±1.60	23.5±6.6	21.3±6.0	27.4±7.7	16.4±4.6	13.4±3.8	15.5±4.4	13.8±3.9
GIT	N/A	N/A	N/A	N/A	9.0±3.2	8.3±2.9	N/A	10.5±3.7
NOAA1	4.97±0.89	24.2±4.4	16.7±3.0	17.8±3.2	10.0±1.8	9.8±1.8	13.3±2.4	12.0±2.2
NOAA2	4.84±0.87	22.7±4.1	N/A	22.7±4.1	15.3±2.8	12.3±2.2	15.3±2.8	13.1±2.4
TVAG	6.65±2.40	23.0±8.3	20.8±7.5	27.5±9.9	15.9±5.7	13.3±4.8	15.7±5.7	14.2±5.1
TVAM	6.07±2.19	23.2±8.3	22.4±8.1	29.4±10.6	17.0±6.1	13.6±4.9	14.7±5.3	13.5±4.9
Mean [†]	5.79±0.82	22.8±0.91	21.0±2.0	26.9±3.1	16.2±0.8	13.4±0.9	15.5±0.8	13.9±0.8

The averaging periods are given as hour of the day (LT). All values are in ppbv. N/A indicates that data are not available. Uncertainties for methods are defined in text.

^{*}Uncertainty of sum calculated as RMS of method uncertainties.

[†]Mean does not include GIT or NOAA1 data. Uncertainties are 95% confidence limits on the mean.

increased by 5% to compensate for the offsets in those data sets versus the average (see Figures 9c and 9d). Then the difference was taken between the adjusted data and the average NO_y measurements and compared to the measured HNO₃ and NO₃⁻. Thus in Table 5 at 1400-1500 the GIT measurement of 9.00 ppbv increased to 11.3 ppbv and the NOAA1 value of 10.0 ppbv increased to 10.5 ppbv, while the mean of the other five points was 16.2 ppbv. The difference between the averaged NO_y and adjusted GIT is 4.9 ppbv and for adjusted NOAA1 is 5.7 ppbv. The sum of HNO₃ and NO₃⁻ at this time is 4.8 ppbv which is within 2% of the underestimated NO_y from GIT and within 15% of the underestimated NO_y from NOAA1. For the period 1600-1700 underestimated NO_y from (adjusted) GIT is 3.0 ppbv and from (adjusted) NOAA1 it is 3.1 ppbv, while the sum of HNO₃ and NO₃⁻ is 3.3 ppbv. This clearly suggests that the GIT and NOAA1 converters were not efficient enough to convert the less tractable NO_y species. Although the long (~60 cm) Teflon NO_y inlet tube on the GIT system may have been responsible for some of the HNO₃ loss, with the available data we cannot assess the magnitude of that loss process compared to possible converter inefficiency. For the NOAA1 converter, though, the inability to determine HNO₃ and nitrate is doubtless due to converter inefficiency since the NOAA1 and NOAA2 converters (and inlets) were identical and the latter operated efficiently.

The data in Table 5 indicate that NO_y measured during this period was accounted for by the NO_y species separately measured, given all of the uncertainties. When NO_y was mostly NO_x (0700-0800, 1900-2100, 2300-0100) the difference between the NO_y sum and the NO_y average was 0.3 to -1.2 ppbv, or ~±6% relative to NO_y. When NO_x/NO_y was low (1200-1300, 1400-1500, 1600-1700) the difference was 0.8 to 3.4 ppbv, or 6-12% relative to NO_y. As shown in Table 5 the total RMS uncertainty on the sum of the NO_y species was 11%, similar to the uncertainties of the average NO_y data. Thus any of the observed differences during this photochemically active period can be accounted for by measurement uncertainties. Comparing all 8 data points of the NO_y sum to the mean NO_y with a t-test showed that the mean difference was not significantly ($p=0.05$) different from zero. However, the fact that there was no statistical disagreement between measured NO_y and the sum of the NO_y species is not the same as saying there was agreement. Even when NO_y was >80% NO_x differences of 6% were found, and this may be the best that can be done with the current methods. For this type of budget analysis to be most useful, total uncertainties in all of these methods needs to be reduced and the frequency of measurement of HNO₃ needs to be increased.

The precision of the NO_y methods, measured as the scatter of the five measurements relative to the mean, was generally quite good. The ND histograms in Figure 9 (Figures 9a, 9b, 9e, 9f, and 9g) show that virtually all of the measurements from those, albeit limited, data sets were within ±20% of one another. This can be viewed as an approximate 3σ precision of replicate NO_y measurements. Similarly, the 1σ RSD of the mean of five averaged NO_y measurements (Table 5) under a wide range of NO_x/NO_y ratios yields estimated precision of the order of ±10%. These two estimates are quite similar to each other. An assessment of the accuracy of an NO_y measurement is another matter. Even though these are independent measurements of NO_y, the accuracy of the NO_y techniques still cannot be assessed on an absolute basis because of the possibility of systematic effects that all of the methods are

subject to, such as inlet losses and converter problems. Some indication of accuracy is provided by the 6-12% level of agreement between the average NO_y data and the sum of the separately measured compounds for the one episode discussed above. On the other hand, there may be substantial differences with sampling location since significant (>25%) disagreement has been seen at other, more remote, sites where more aged air was sampled [Fahey *et al.*, 1986; Crosley, 1996; Williams *et al.*, 1997]. This may not mean that the NO_y technique is inaccurate; it may be that not all of the NO_y species are known and measured. However, in the urban and suburban (i.e., less aged) air masses encountered during this study, we conclude that most of the techniques tested were adequate for the determination of NO_y.

4.3. Spike Test Results Compared to Ambient Air Measurements

If the average results from the spike tests (Table 4) are considered to be reliable, then those data should provide a measure of the comparability of the different ambient air NO_y data sets. The spike results showed that all of the systems should measure comparable levels when NO_x is a substantial fraction of NO_y. This appeared to be the case (after adjusting the GIT data by 25%) not only as shown by Plate 1a but also for virtually all of the measurements. For both small scale variations and large and rapid changes, when NO_x/NO_y >60% all of the NO_y instruments provided similar data. Moreover, the same result should apply when PAN or other peroxy-carboxylic nitric anhydrides are a large fraction of NO_y since these compounds behave virtually identically to NO₂ in the very hot (>300°C) environments of any of the converters. And, like NO₂, the uptake of these species on surfaces is small thus there will be little loss on inlets.

Spike data from the more difficult to convert species, however, suggest that some systems will not agree during ambient measurements. The average results for NPN in Table 4 suggest that the GIT, NOAA1, and NOAA2 converters will underestimate NO_y, but since alkyl nitrates are typically only a small fraction of NO_y [Buhr *et al.*, 1990] the effect should be minimal. On the other hand, for HNO₃ the Table 4 data indicate potential problems for BNL, GIT, NOAA1, NOAA2, and, to a lesser extent, TVAG. Except for the GIT and NOAA1 data, these results do not seem to hold for the ambient air measurements as described above for July 1. When HNO₃ was 20-25% of NO_y (at 1200-1300 and 1400-1500) and easily measurable differences in NO_y should have been apparent, all of the NO_y data (except for GIT and NOAA1) clustered together.

The reasons for this lack of consistency between the spike results and the ambient air data are likely related to the spike tests. Although unstable output from the spike gas sources is not likely a factor based on the measured constancy of the source controlling parameters (e.g., temperatures, flows, pressures, etc.) and the TVAM and TVAG spike test results, subtle (but perhaps significant) differences in how the spike tests were administered could have been responsible. Such factors as how far the spike source tube was placed in an inlet, the length of time needed for a spike gas to condition the inlet tubing walls, changes in the ambient air environment (i.e., temperature, humidity, aerosol loading or composition, etc.) during and between spikes, imprecision in the determination of a spike level due to large and changing NO_y backgrounds, and perhaps other factors all determined how reliable the spike

tests were. Some of these factors no doubt contributed to the super-unity recoveries seen in the NPN and HNO₃ tests. In retrospect, the spike test levels probably should have been made much larger than the expected ambient NO_y mixing ratios to improve the precision of the tests. Administering the tests in zero air would not have helped because higher conversion efficiency is found when the tests are done in that dry-air matrix than when the same converter is tested in ambient air. At least this was true for the NOAA1 and NOAA2 Au converters for this study.

4.4. Comparison Between Au and Mo Converters

The last point for discussion is an assessment of the differences, if any, between the two types of converters. For this comparison the NOAA1 Au converter and the GIT Mo converter are excluded because of the problems already discussed. This leaves two, quite similar, Au tube/CO reductant converters with the only significant difference being the temperature of operation. The NOAA2 tube was held at 300°C and the TVAG tube was held at 320°C. Of the three Mo converters, two (ESE; TVAM) were obtained from commercial sources and one was custom built (BNL). Again, there were differences in the temperature at which these devices were controlled (BNL at 350°C; ESE at 375°C; TVAM at 340°C), but there were also differences in inlet design. The data in Table 2 (1174 points) for each group (Au versus Mo) were averaged and plotted against each other. The result is shown in Figure 12 where the solid line is that of one-to-one correspondence and the dashed line is the weighted linear least squares fit line. The weights used were the inverse of the standard deviations of each averaged point. Standard deviations of Au mean values were comparable to those of Mo mean values.

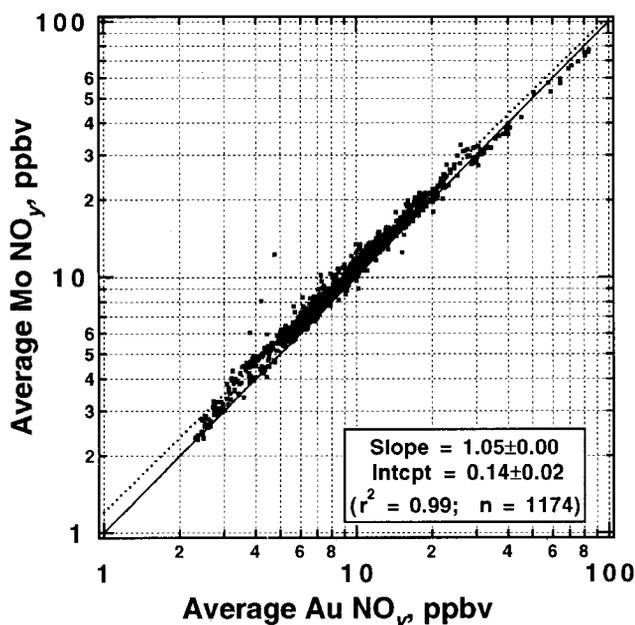


Figure 12. Average NO_y measured by Mo converters (BNL; ESE; TVAM) plotted versus average NO_y measured by Au converters (NOAA2; TVAG). The solid line is that of one-to-one correspondence, and the dashed line is that fitted to the data by weighted linear least squares. The fitted line parameters and associated uncertainty are shown in the box.

As expected, there was a high degree of correlation between the data sets (r^2 is near unity) and very small uncertainty on the slope and intercept. The plot indicates only a small difference between the Au and Mo converters for this data set, although there is a clear tendency for the Mo NO_y measurements to be higher than the Au NO_y measurements. Elimination of the small positive offset seen in the BNL data (Figure 9b) had little influence on the parameters from the least squares fit (slope: 1.04; intercept: 0.12). A possible reason for the Au-Mo difference may arise from aerosol effects related to design differences between the tube-type Au converter and the mesh-type Mo converters. By design, nitrogen-containing aerosols contact the heated Mo mesh and are converted to NO, but the open-bore design of the Au converters should pass the majority of aerosols. However, no correlation was seen when the difference in NO_y between Au and Mo converters was plotted versus aerosol nitrate. On the other hand, the small difference between the converters seen in Figure 12 is well within the uncertainties in the NO_y measurements. Thus we conclude that the converters were virtually equivalent when operated in the high-NO_y urban/suburban environment near Nashville during this study. However, in rural or remote areas where NO_y levels are 1 ppbv or less (sometimes much less) the difference seen in Figure 12 could become quite significant. Since many NO_y measurements are conducted where NO_y levels are very low (i.e., from aircraft) as opposed to in urban areas, it seems prudent that NO_y instruments be rigorously compared at those lower levels.

5. Summary and Conclusions

The results from this study indicate that NO_y at levels typical of urban locations can be determined adequately by currently used NO_y converters. However, since NO_y consisted mostly of NO_x for much of the time, this study did not provide a rigorous test of NO_y instruments. Also, generally high and variable levels of NO_y (2 - 100 ppbv) limited interpretation of the spike test results because of poor precision. Nevertheless, sufficient data were collected to allow the following conclusions to be made.

1. Some loss of conversion efficiency was found with two of the seven converters. The GIT and NOAA1 converters did not measure the same levels of NO_y as the other tested systems when photochemical conversion of NO_x to more oxidized NO_y species occurred. For the NOAA1 converter this was clearly due to inefficient NO_y conversion at low NO_x/NO_y ratios rather than inlet losses, since the very similar NOAA2 converter provided results that were reasonably consistent with the majority of the data. (The NOAA group extensively evaluated these converters upon return to the laboratory and found that the NOAA1 converter could not be returned to 100% efficiency, regardless of the cleaning procedures used.) The GIT system appeared to have a systematic problem since those data were consistently lower (25%) than the rest of the measurements. When this offset is artificially accounted for, the GIT data were in accord with the other data but only when NO_y was substantially comprised of NO_x. The offset has been attributed to problems with the calibration system, which was redesigned after this study. During periods of high photochemical activity larger differences between GIT and average NO_y data were seen. Losses of more oxidized NO_y species in the inlet tubing and/or inefficient conversion were the probable reasons for that difference. Aside from the GIT and NOAA1

instruments, no other losses of conversion efficiency were found. The consequence is that measurement of NO_y can be made in an urban outflow region, but requires constant attention from experienced personnel.

2. The results from the spike tests for some instruments (ESE, TVAG, TVAM) were consistent with the ambient air data, but for other systems (BNL, GIT, NOAA1, NOAA2) they were not. For BNL, NOAA1, and NOAA2, the low average recoveries from the HNO₃ tests were approximately comparable, but only the NOAA1 converter measured low NO_y when HNO₃ was a sizable fraction of NO_y (20-25%). No reason was found for the inconsistent BNL or NOAA2 results. The GIT converter showed higher recovery from the HNO₃ spike tests than BNL or NOAA2 (especially when the systematic offset was accounted for) but found uniformly lower NO_y than the BNL or NOAA2 converters when the ambient HNO₃ level was high. On the other hand, when the ambient NO_x/NO_y level was greater than about 0.6 all of the instruments measured NO_y levels consistent with one another, though, again, the GIT data needed to be corrected for the observed average offset. These results were in good accord with the spike test results. It appears that a significant reason for the ambiguous results between spike tests and ambient air data was the reduced precision of the spike tests due to the large and varying NO_y levels found at this site. Other factors related to how the tests were conducted, such as the time required to condition inlet lines, also may have contributed to the observed inconsistencies.

3. A small difference was evident between the averaged NO_y data from Mo converters and that from Au converters. Though the average NO_y measured by three Mo converters was 5% higher than NO_y measured by two Au converters, the difference was within the uncertainties of the measurements. For the levels of NO_y measured at this urban/suburban site, the difference between Au and Mo converters is negligible, but for measurements of low NO_y levels (<1 ppbv) at remote locations the difference might be significant.

4. Finally, some general observations need to be made. The differences observed in NO_y measured at this site were attributable to specific performance problems only because sufficient ancillary and redundant NO_y data were available. If, for example, the GIT or NOAA1 converters only had been used (and without the benefit of spike tests or ancillary NO_y measurements) then incorrect results would have been reported. Conversion efficiency for NO_y catalysts can depend on any number of parameters, such as cleaning procedures, history of the catalyst, nonuniformities in catalyst temperature, and sampling matrix (e.g., temperature, humidity, aerosols) to name a few [Fahey et al., 1985; Kliner et al., 1997]. It is imperative, then, that constant tests and checks of these systems be performed during the measurements to ensure data of the highest quality. Further, these differences point out the need to acquire and evaluate data in near real time. Since nothing can be done to correct the data after the experiment is over, any problems with the NO_y measurements (i.e., low conversion efficiency or interferences from non-NO_y species) must be dealt with while the data are being collected. Certainly redundant NO_y measurements can be very helpful for determining whether corrective actions need to be performed or if errors arise during poststudy data processing, as was seen here with the TVA data. However, the primary evaluation of the robustness of NO_y measurements should be with the individual NO_y species themselves and with species known to

interfere (e.g., NH₃, HCN). For routine calibrations and checks, species such as NO₂ or NPN are useful since they are themselves NO_y species and they are convenient to handle in gas delivery systems. However, for the most accurate determination of converter efficiency, HNO₃ must be used for field evaluation tests since it is this NO_y species that is the most difficult to determine with existing NO_y instrumentation.

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