AMBIENT GASEOUS AMMONIA: EVALUATION OF CONTINUOUS MEASUREMENT METHODS SUITABLE FOR ROUTINE DEPLOYMENT

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Final Report

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ABSTRACT AND KEY WORDS

Measurement of gaseous ammonia at low ambient levels has presented a significant challenge to atmospheric chemists and air pollution scientists for many years. While a number of measurement methods have been attempted and described in the literature, various shortcomings have prevented the adoption of any known method for routine continuous ambient measurement of gaseous ammonia. The present study seeks to fill that gap in two ways. First, commercially available continuous methods are tested in the laboratory against each other, calibration standards, and established research methods to establish instrument precision, accuracy, and operational characteristics, including instrument time response. Based on the results of the laboratory intercomparison exercise, the Ion Mobility Spectrometer (IMS) was selected for field deployment. This deployment took place from late February through the end of May in 2006 at the Pinnacle State Park research station in Addison, NY. Continuous low-level measurement of gaseous ammonia has been demonstrated for this three-month period, with a range of concentrations from below detection limit to almost 6 ppb (5.82 ppb) and with a mean concentration of 1.06 ppb and a median of 0.87 ppb. While there are still problems and pitfalls associated with continuous and routine low-level measurement of gaseous ammonia, progress has been made and widespread deployment should be possible in the near future.

Key Words:
ammonia
measurement methods
atmospheric chemistry
air pollution
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EXECUTIVE SUMMARY

Gaseous ammonia is a ubiquitous atmospheric species that is involved in numerous processes important to air pollution and human health and welfare. Understanding levels of gaseous ammonia is absolutely critical for developing strategies to control $PM_{2.5}$. Measurements of ammonia are required to understand the formation and transformation of particulate matter; and to help quantify types and magnitudes of sources of ammonia to the atmosphere. Unfortunately, measurements of this critical trace gas are neither reliable nor routine. Gaseous and particulate nitrogen species play critical roles in nearly every aspect of atmospheric chemistry and air quality research. Understanding the ambient levels and chemistry of ammonia in the gas and particle phase is critical for the development of State Implementation Plans (SIPs) under the National Ambient Air Quality Standards (NAAQS).

The work was undertaken specifically to address the measurement issues associated with gaseous ammonia. It is fair to say, that in spite of its very simple molecular structure, routine and accurate real time ammonia measurements have been few and far between. The goals of the project were to assess the available measurement technologies for routine atmospheric measurement of gaseous ammonia, to compare suitable candidate techniques with established research methods in a laboratory intercomparison, and to operate at least one candidate routine method for a three-month period in the field. These three goals were met, and the details are contained in this report.

There are many ways to detect and measure ammonia, and many of the methods have adequate time response and sensitivity for atmospheric purposes. The difficulty in most cases is the artifacts and/or interferences inherent in the sampling and handling of the ambient level ammonia. Ammonia is second only to water vapor in the strength of its hydrogen bonds and in its tendency to adsorb and/or react with any and all surfaces, be they passivated, treated, or otherwise. One major result of this work, while perhaps not entirely new, is the greater realization that the only way to obtain reliable, repeatable, and sensitive measurements of gaseous ammonia is to strictly minimize the sampling and handling of ammonia itself. Put another way, any technique that seeks to draw gaseous ammonia through tubes, valves, and flow devices is virtually certain to suffer from unacceptable levels of artifacts.

The laboratory work for this project involved the comparison of six different measurement methods at low part-per-billion levels in a (mostly) controlled setting. The methods included research methods, which are methods requiring significant expertise and ongoing operational skill, and commercial instruments, which, in principle, should be suited for routine deployment with only moderate expertise and minimal ongoing operational demands. The instruments were the Tunable Diode Laser absorption spectrometer(TDLAS), the wet scrubbing Long Path Absorption Photometer (LOPAP), the Wet Effusive Diffusion Denuder (WEDD), the Ion Mobility Spectrometer (IMS), the Nitrolux laser acousto-optical absorption analyzer, and a modified chemiluminescence analyzer. With the exception of the modified chemiluminescence analyzer, the instruments performed well, and under stable calibration conditions, they generally agreed to within about 25% of the expected calibration value. Instrument time response is shown to be sensitive to measurement history as well as sample handling materials and is shortest for the TDL. The IMS and Nitrolux are commercial instruments used without modification from the manufacturer. These two instruments have significantly slower time response than the TDL (especially in the case of the Nitrolux) and exhibited measurement biases of approximately +25% (IMS) and -25% (Nitrolux). The LOPAP and WEDD instruments, both research instruments using wet chemical methods, performed well in the calibration tests in terms of the accuracy of measured concentrations, but the WEDD instrument suffered from significantly slower time response than the LOPAP.

Based on the results of the laboratory intercomparison exercise, the Ion Mobility Spectrometer (IMS) was selected for field deployment. This deployment took place from late February through the end of May in 2006 at the Pinnacle State Park research station in Addison, NY. Continuous low-level measurement of gaseous ammonia has been demonstrated for this three month period. The IMS instrument provided adequate sensitivity to detect and quantify the sub-ppb levels of ammonia often encountered at the measurement site. Measurements showed a range of concentrations from below detection limit to almost 6 ppb (5.82 ppb), with a mean concentration of 1.06 ppb and a median of 0.87 ppb. For this ammonia analyzer, the issue of time response, and more specifically, the ability of the analyzer to accurately track rapid up and down changes in ammonia concentrations, requires further evaluation.

In spite of our poor experience with the chemiluminescence technique for ammonia measurement, other scientists have learned how to correct the problem we encountered in our laboratory exercise (Hansen et al., 2006). This method, when properly applied with appropriate denuders and multiple catalytic converters, has the major advantage because the ammonia to be measured is rapidly converted to NO (nitric oxide), so that sampling and handling of ammonia is all but eliminated. At the same time, additional experience over a longer term deployment of the IMS at our field site (and in particular an apparent decay of ambient ammonia during the sampling and handling prior to detection) has led us to question the suitability of this technique for long term deployment. This unresolved issue with the IMS used for extended periods, possibly due to sample handling issues in the analyzer, points out the difficulty of measuring low-level ammonia accurately and routinely. They also encourage us to make the following tentative recommendation – *one can expect good results from an IMS instrument in the field for at least three months, but longer deployments may suffer from an as yet unknown deterioration; however - properly implemented, the denuder difference/catalytic conversion with chemiluminescence detection method appears to be the best method suitable for long-term routine deployment.*

1 LABORATORY INTERCOMPARISON OF REAL-TIME GASEOUS AMMONIA MEASUREMENT METHODS

1.1 INTRODUCTION

Ammonia (NH_3) gas plays a number of important roles in atmospheric chemistry, aquatic chemistry, and terrestrial ecosystems (Asman et al. 1998; Krupa 2003; Aneja et al. 2006). As a result, many measurement methods for NH_3 have been developed (Genfa et al. 1989; Mennen et al. 1996; Pryor et al. 2001; Williams et al. 1992; Fehsenfeld et al. 2002), though with few exceptions, ambient measurement of NH_3 has remained a "research activity" – requiring equipment that is often delicate and expensive, and labor-intensive. Nevertheless, the United States Environmental Protection Agency has designated gaseous NH_3 as a target pollutant for measurement at roughly 75 NCORE level 2 multi-pollutant sites nationwide (EPA 2005). This poses a significant challenge since ambient NH_3 levels vary from background levels of < 50 ppt to concentrations 1000 or even 10,000 times greater near agricultural or forest fire sources (Krupa 2003). Also complicating matters, NH_3 forms strong hydrogen bonds with water (and itself). Interaction of NH_3 in the ambient sample with tubing and other parts of the instrument can lead to irreversible loss or to adsorption and desorption effects that produce higher backgrounds and memory effects (Fehsenfeld et al. 2002). A number of methods have attempted to use the affinity of NH_3 for water to their advantage by capturing NH_3 into liquid water and detecting the ammonium NH_4^+ using various methods (Pryor et al. 2001; Trebs et al. 2004; Genfa and Dasgupta 2000). This does not always eliminate all potential losses, since NH_4^+ can also volatilize (Sorooshian et al. 2006) or interact with surfaces (D. Orsini, personal communication).

We report a laboratory intercomparison of six independent real-time continuous measurement methods for NH_3 undertaken to assess the level of comparibility of research methods with each other and the commercial methods (both in terms of absolute concentrations and time response) and to evaluate the commercial methods as candidates for routine deployment at atmospheric chemistry research stations and air quality monitoring sites.

1.2 METHODS AND INSTRUMENTS – LABORATORY INTERCOMPARISON

We chose to undertake a laboratory intercomparison in order to test responses to concentration spikes and zero points and the time responses of the instruments in a controlled setting. However, ambient air was also introduced into the manifold for significant periods of time. Sampling issues may mean that concentrations in the sample manifold did not reflect the "true" NH_3 concentrations in the outside air (due perhaps to re-partitioning of aerosol ammonium nitrate, for example), but since all instruments drew from the same manifold, all will be similarly affected by this. The instruments and manifold system are described below.

1.2.1 AirSentry IMS Ammonia Analyzer

Details of the IMS technique are given in Hill et al. (1990); and Bacon et al. (1998). The technique uses ionization of the NH_3 molecule followed by electrostatic extraction of its ions into a drift chamber and detection at a collector plate. The shutter grid producing the extraction field is pulsed periodically to allow ions into the drift tube; and ion time-of-flight is used to identify the ammonia ion. Confirmation of the ion identification/ quantification is obtained through the measured addition of a dopant molecule (in this case dimethyl methylphosphanate – $(CH_3)_3PO_3$).

The Ion Mobility Spectrometer (IMS) used in this comparison was purchased from Particle Measuring Systems (Boulder, CO). Detection selectivity is achieved through specificity of a semi-permeable membrane that allows ammonia to pass into the drift chamber region, and through the consistent time-of-flight of the ammonia ions as they traverse the stable drift flow. The AirSentry uses eight individual time-of-flight spectra to produce each sample concentration, which equates to an averaging period of less than 0.2 seconds. Samples may be further averaged using a user selectable smoothing factor (eight was used herein), which calculates a rolling average concentration value.

1.2.2 Nitrolux 200

The Nitrolux 200 was manufactured by Pranalytica, Inc. (Santa Monica, CA). The laser photoacoustic spectroscopy method involves specific absorption of radiation by NH_3 molecules, followed by collisional deactivation of NH_3 and simultaneous heating of the gas in the sample cell and detection of the acoustic energy generated using a sensitive microphone.

The Nitrolux system uses a carbon dioxide molecular gas infrared laser, which is tuned to an absorption feature of NH_3, then wavelength (or frequency) modulated on and off the absorption feature. The photoacoustic absorption method uses a modulation frequency in the range 10-100 Hz. Data points are generated every 40 to 43 seconds. The sensitivity of the technique is determined primarily by laser power and the design of the acoustically resonant cell. Interference is minimized by careful selection of a laser wavelength that is isolated from absorption transitions of potential interferents. The manufacturer guarantees calibration stability for 6,000 hours after a factory calibration. The laboratory intercomparison exercise was completed less than 1,500 hours after a factory recalibration.

1.2.3 Tunable Diode Laser Absorption Spectrometer (TDLAS)

The TDLAS was built by Aerodyne Research, Inc. (Billerica, MA) (see description in Li et al. (2004); Li et al. (2006)). The system consists of a liquid nitrogen cooled dewar that holds the laser and detector, an optical bench (including a reference cell) for directing the beam, a Herriott-type multipass absorption cell, and computer controlled electronics to control the system. The absorption cell provides a path length of 153.5 m in a volume of 5 liters, and is kept at a stable pressure of 3.3 kPa (about 25 Torr) to reduce pressure broadening of the absorption lines and allow highly specific identification of NH_3 absorption features. A wavelength of 9.3847 μm (1065.5654 cm^{-1}) was used here. This feature is a triplet of lines, and the strongest line has an integrated cross section of 2.60×10^{-19} cm^2 $molecule^{-1}$ cm^{-1} (Rothman et al. 1998). The accuracy of concentration measurements using the TDLAS is fundamentally determined by the accuracy of the line strengths, as well as additional uncertainties in the path length, pressure, temperature, diode mode purity, and line shape model. These factors are discussed in Li et al. (2006), and the reported accuracy of the TDLAS for NH_3 is better than 14%.

TDLAS measurements often use background subtraction to improve instrument performance (Li et al. 2006). Background subtraction can remove low frequency optical fringing noise – frequently a major source of sensitivity limiting noise. This correction scheme is implemented by alternating measurements of ambient air and zero air, all within one minute. The "zero air" in this case was produced by switching the sample flow to pass through a citric acid coated denuder before entering the sample cell. Unfortunately, a single denuder was unable to quantitatively remove all NH_3 from the background sample – our experience with citric acid denuders is that they do not fully reduce gaseous ammonia to zero for this instrument. After this discovery partway through the intercomparison exercise, the TDLAS was operated without background subtraction. For this reason, TDLAS data from the beginning of the exercise until 9/22/05 are expected to be biased low.

1.2.4 Long Path Absorption Photometer (LOPAP)

The LOPAP is a research instrument built by Jian Hou and Xianliang Zhou at the University at Albany School of Public Health. The method is based on aqueous scrubbing of NH_3 (and aerosol NH_4^+) by wetted glass frit impactors, followed by derivatization of the aqueous ammonium into a highly light-absorbing indophenol, and quantification of the derivatized NH_3 with a long-path absorption spectrophotometer (Bae et al. 2007). The system measures NH_3 by difference in a two-channel system. The first measures NH_x ($NH_3 + NH_4^+$), while the second uses a citric acid denuder to remove gaseous NH_3, resulting in a measure of aerosol NH_4^+ only. Thus, NH_3 is the difference between these channels.

Each channel draws 2 L/min over a glass-frit impactor that is continuously wetted with deionized water. NHx, in the sample, is scrubbed and dissolved into the water membrane formed on the surface of the porous frit plate. To reduce the measurement blank, ion-exchange columns packed with polystyrene divinylbenzenesulfonic acid are connected online to reduce residue NH_4^+ in the deionized scrubbing water. The solution passes through a gas-liquid separator and into a reaction coil where it reacts with sodium salicylate and alkaline sodium hypochlorite to form the indophenol. The derivative is analyzed at 660 nm by a long path absorption photometer system consisting of a fiber optic optical light source (FO-6000, WPI), a liquid waveguide capillary cell (LWCC, 1 m, WPI), and a USB2000 miniature fiber optic spectrometer (Ocean Optics). A three minute sample cycle consists of 1.5 minutes measuring total NH_x and 1.5 minutes measuring aerosol NH_4^+, so that total NH_x, aerosol ammonium, and gaseous NH_3 are recorded every three minutes. The lower detection limit of 9 nM is estimated based on a 3:1 signal to noise ratio of samples containing NH_4^+ at a concentration level near the blank. This is equivalent to about 30 pptv for atmospheric NH_x in ambient air with the air flow of 2 L/min and the scrubbing flow rate of 0.24 ml/min.

1.2.5 Wet Effluent Diffusion Denuder (WEDD)

The wet effluent diffusion denuder method was developed by Sørensen et al. (1994). The two instruments used in this intercomparison are patterned after these systems and have been extensively calibrated and deployed for measurement of NH_3 (Pryor et al. 2001; Pryor et al. 2004). As the name implies, the method employs an annular denuder continuously wetted with water to capture NH_3. The water and NH_4^+ leave the diffusion denuder tube and are mixed with *o*-phthaldialdehyde (OPA) and sulfite in a heating coil, resulting in a reaction that produces a fluorescent product, which is measured in situ. The diffusion scrubbers have an inner diameter of 4 mm and a length of 50 cm, allowing sufficient time for the NH_3 gas to diffuse to the water surface, but insufficient time for significant contamination due to particle diffusion and trapping (Pryor et al. 2001). Liquid flows of water, sulfite, and OPA are controlled by a peristaltic pump; the water flow to the diffusion denuder is 0.15 ml/min. Data are collected every second and are reported as minute averages. The estimated minimum detection limit is ~ 1 nmole m^{-3} (or ~25 pptv at 298 K and 1 atm) (Pryor et al. 2004).

1.2.6 Chemiluminescence Analyzer

The chemiluminescence system built for these experiments was a hybrid system based on a Thermo Electron 42C-TL trace level NO_x analyzer chemiluminescence detector along with two catalytic converters for the conversion of gas phase nitrogen compounds to nitric oxide (NO), which is the species detected by the analyzer. A heated molybdenum converter (Thermo Electron) converted oxides of nitrogen to NO, and a Model 100N Thermal Oxidizer (Measurement Technologies) converted reduced nitrogen species to nitrogen oxides. The 30 second measurement period consists of 10 seconds measuring detector background, 10 seconds measuring total oxides of nitrogen (NO_Y), and 10 seconds measuring total reactive nitrogen. The calculated difference between the total gaseous reactive nitrogen and the total oxides of nitrogen is actually the total reduced nitrogen species, but in the absence of interfering basic gases (such as organic amines or the like), this difference can be operationally attributed to NH_3. This method has been successfully employed for relatively high levels of NH_3, such as those measured near sources (McCulloch and Shendrikar 2000), and more recently for ambient levels in the southeastern U.S. (Hansen et al. 2003; Hansen et al. 2006).

While the analyzer configured with the two converters worked acceptably during calibrations with either NO or NH_3, it reported results that were clearly wrong (such as large and negative values for the reduced nitrogen concentrations) during ambient sampling periods. We later determined that the Model 100N Thermal Oxidizer converted NH_3 to NO efficiently, but it did not convert higher oxides of nitrogen to NO efficiently. This means that the signals from samples passing through the Model 100N were not total reactive nitrogen as planned. This failure to covert all higher oxides of nitrogen to NO by this converter led us to eliminate this instrument from the intercomparison. Hansen et al. (2006) dealt with this problem for their system by adding a second heated molybdenum converter downstream of their thermal oxidizer on their total reduced nitrogen channel.

1.2.7 Sample Manifold

The manifold was a 25 mm I.D. heated glass tube of nearly 4 m total length fitted with ten 7 mm I.D. ports over the last 1.5 m of the manifold. The manifold tube extended about 10 cm through an opening in the outside wall to allow the sampling of ambient outside air. The downstream end (past all the sample ports) of the manifold tube was coupled to a PVC Tee, which contained a Vaisala HMP 35A temperature and relative humidity probe. The tee then connected to a 28 mm O.D. Tygon tube that was coupled to a blower box containing a voltage controlled blower (Ametek Windjammer Bypass Blower). The blower was capable of exhausting air volumes ranging from less than 10 L/min to greater than 70 L/min through the manifold.

The manifold ports were spaced 15 cm apart over the middle portion of the manifold tube. Each instrument was connected to the manifold with a roughly 2 m long section of 6.3 mm O.D. PFA Teflon tube. Table 1-1 lists the manifold positions used during the intercomparison. Manifold positions for four of the instruments were changed early on in the study for a seven hour period to check for stability of concentrations with sample ports. No measurable differences were observed due to the change in ports, so no further tests were performed, and manifold sample ports remained stable for the rest of the study. As a test, one instrument sample line was replaced with a 6.3 mm O.D. stainless steel tube, but the stainless steel exhibited greater surface losses than the PFA, so PFA was used exclusively for experiments. The ports not used for instruments or calibration gases were plugged.

Manifold Port	Instrument or Function	Flow Demand (drawn from manifold)	Instrument Detection Limit (and Integration Time)
1	Calibration Gas	N/A (flow into manifold when active)	N/A
2	Spare	N/A	N/A
3	Spare	N/A	N/A
4	Pranalytica Nitrolux 200	0.3 L/min	200 ppt (~ 1 minute)
5	WEDD #1	1.5 L/min	25 ppt (1 minute)
6	WEDD #2	1.7 L/min	25 ppt (1 minute)
7	AirSentry IMS Analyzer	2.5 L/min	70 ppt (< 1 minute)
8	LOPAP	4 L/min	30 ppt (3 minutes)
9	Chemiluminescence	2.5 L/min	N/A
10	TDLAS	4 L/min	100 ppt (1 second)

Table 1-1. Sample manifold ports, function or instrument associated with that port, and flow demand associated with the instrument.

The manifold was heated using a heating cable and temperature controller (Tyco Raychem). The manifold, heating cable, and temperature sensor were wrapped with foam pipe insulation to help the system maintain a constant temperature. Operationally, the heating cable, sensor, and controller kept the portion of the sample manifold with the ports within one or two degrees Celsius of the 40º C set point. The 40ºC set point was chosen to reduce the amount of water vapor sticking to the manifold walls, and thereby reduce the loss of ammonia. The elevated temperature would tend to dissociate aerosol ammonium nitrate, but the goal was stable gaseous ammonia, whether from gaseous or aerosol sources.

1.2.8 Calibration System

We designed the calibration system to be capable of supplying 35 l/min to the manifold for calibrations (the instruments drew a total of about 16.5 l/min) and to maintain the relative humidity in the lines at above 30%. During calibrations the blower control voltage was set so that 10-12 L/min were exhausted through the blower, and an excess flow of 6.5-8.5 L/min flowed out through the sample inlet. The excess flow was necessary to assure that no ambient air infiltrated into the calibration air.

Producing scrubbed zero air for the calibrations at a flow rate of 35 L/min without any traces of NH_3 was a difficult task – and we were not totally successful in this regard. Zero air was generated initially as oil-free compressed air, which was passed through a membrane dryer to bring it to a consistently low dew point, then delivered to a Thermo Electron Model 111 Zero Air Source. We followed the Model 111 with an additional four scrubber cartridges in the following order: drierite, activated charcoal, Purakol AM, and Purafil, with an additional 2 cm of Purakol AM at the finish. The best we could do with this scrubber-based system was to deliver humidified zero air with NH_3 concentrations between 0.5 and 1 ppb. This is similar to the results obtained by Williams et al. (1992) when they attempted to scrub ambient compressed air. The failure to produce truly NH_3-

free air for these tests does increase the uncertainty in our results, but it does not otherwise affect the results reported below.

For the experiments presented here, the NH_3 calibration source was a mixture of 3.55 ppm NH_3 in N_2 in an aluminum high pressure cylinder from Scott- Marrin (Riverside, CA). Using this standard, “high” concentrations of 20 to 40 ppb and step changes in concentration were generated. A second ammonia calibration source used - a permeation device (certified permeation rate of 45.1 ng/min; VICI Metronics, Poulsbo, WA) - produced a single NH_3 concentration of 1.7 ppb at a total flow of 35 L/min.

The calibration gas was humidified using a sealed PFA Teflon container as a bubbler. Scrubbed zero air passed through a mass flow controller, then into the heated PFA container where it picked up water vapor, then through a secondary container and a PTFE Teflon filter to capture any liquid water before it joined the second calibration gas stream containing the NH_3. The relative humidity of the calibration air, when corrected to the room temperature of 20±1° C (the appropriate sampling temperature for the instruments), was in the range of 35-63%.

In addition to multi-hour calibration experiments, two calibration spikes and one standard addition spike were performed. The calibration spikes provided concentrations of 40 ppb for one hour to the sampling manifold; in the first case starting from “zero” and returning to “zero”, and in the second case starting from 5 ppb and returning to 5 ppb. The ambient spike was a three hour long standard addition of approximately 5 ppb NH_3 on top of the ambient concentration. Only 0.09 L/min of gas from the cylinder mixture was added to the approximately 64 L/min manifold flow for this experiment. Ambient air was sampled from the manifold for two periods of roughly 2 ½ days each, and for a third period of almost a day.

1.3 RESULTS – LABORATORY INTERCOMPARISON

Experiments with all instruments operational began on 9/14/2005 and ended on 9/28/2005. Two hours three days a week were set aside for instrument maintenance and calibration, as required. Intercomparison calibrations from the manifold were typically performed after a period of zero air to allow the instruments to measure a low background. Four calibrations were performed using combinations of concentrations at 5, 10, 20, and 40 ppb from the cylinder mixture, and using the 1.7 ppb level from the permeation device. After the first few calibrations, it was determined that most of the instruments needed many hours (four or more in some cases) to reach stable readings. The last two calibration exercises allowed at least five hours at each concentration.

Data acquisition times were different for the many instruments in the intercomparison. The base reporting period for the TDLAS was one second, and for the LOPAP it was three minutes. The other instruments had base reporting times between these limits. For the purposes of comparison, data from the six instruments presented in this section were averaged (if necessary) to three minutes. This averaging only masks the response time of the TDLAS, since all the other instruments with shorter reporting periods have instrument response times much slower than three minutes, as will be shown below.

1.3.1 Calibrations

Figure 1-1 shows results from three different calibrations. In panel a) the manifold concentration changes from “zero” to 20 ppb at 16:00 on 9/14, stays there until 8:00 on 9/15 when it is changed to “zero” again for one hour; then increased to 20 ppb again at 9:00. The range of responses for this first calibration exercise is almost a factor of two, with the TDLAS and Nitrolux stabilizing near 14 ppb, WEDD1 at 20 ppb, and WEDD2 stabilizing closer to 23 ppb. The IMS measurements are consistently high throughout the intercomparison, and the Nitrolux measurements are consistently low. This may simply point to calibration errors for these instruments. Note the TDLAS was using background correction for this experiment leading to the negative bias. Based on this experiment the TDL is the fastest to respond to the concentration change, followed by the LOPAP. The IMS and WEDD2 show intermediate response times, and the WEDD1 and Nitrolux have quite long response times. During the one hour zero air period near the end of the calibration period, only the TDLAS and LOPAP reach background readings – all the other instruments show a decrease in signal but begin to increase again before reaching

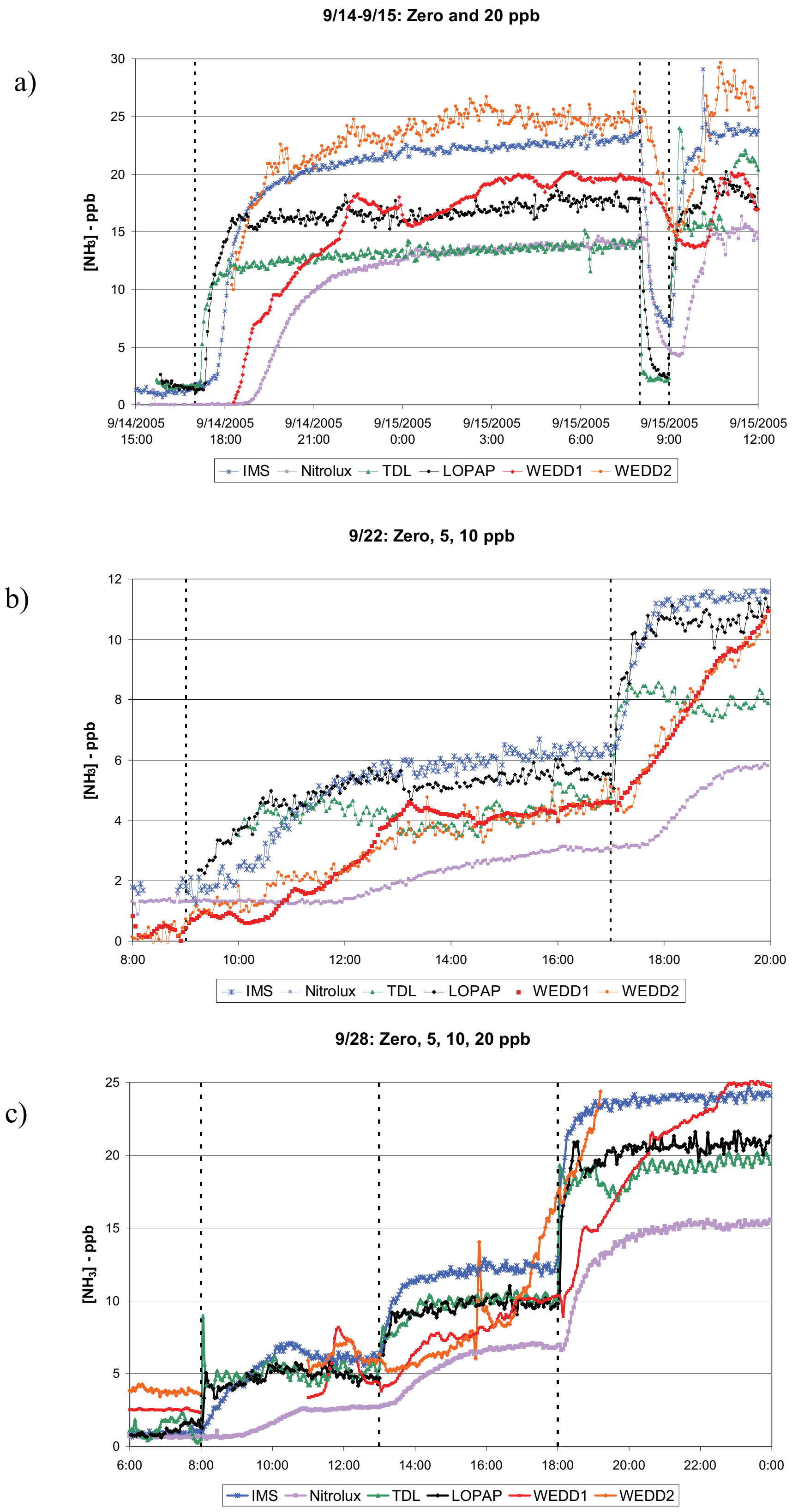

Figure 1-1. **Instrument responses to three different calibration exercises. a) The exercise starts with scrubbed "zero air", followed by 20 ppb for 15 hours, zero air for one hour and 20 ppb for two hours. b) Starting from zero air, the NH_3 concentration is raised to 5 ppb for 8 hours, then to 10 ppb overnight. c) This exercise starts with zero air, followed by 5 hours of 5 ppb ammonia, 5 hours of 10 ppb NH_3, and 20 ppb NH_3 overnight.**

background levels. The failure of some instruments to approach the background "zero" concentrations of approximately 1 ppb in Figures 1-1a and 1-1b, in particular, is due to the relatively short (approximately one hour) periods of zero air flow. The Nitrolux, IMS, and WEDD instruments often required many hours to achieve stable background responses.

In panel b) of Figure 1-1, a 5 ppb concentration was introduced into the manifold at 9:00 followed by a 10 ppb concentration at 17:00. The TDLAS was offline at the beginning of this exercise, and its operation was changed from using background subtraction to no background subtraction at 13:00. All other instruments show a very slow response time to the 5 ppb concentration, which may indicate a particularly long equilibration time for the calibration system and/or manifold in this case. For the 5 ppb calibration standard the LOPAP and IMS derived concentrations were biased slightly high (5-6.5 ppb), while the two WEDD systems and TDLAS slightly underestimated the concentration (4-5 ppb). Figure 1b) shows that, with the exception of the Nitrolux, all the instruments achieved a stable concentration within approximately ±20% of the 'expected' concentrations. For the 10 ppb standard at the end of this calibration the LOPAP, IMS, and WEDD systems all showed slightly higher concentrations than 10 ppb, while the TDLAS measured 8 ppb, and the Nitrolux system measured concentrations below 6 ppb.

The final calibration exercise of the intercomparison involved concentration steps from "zero" to 5 ppb, to 10 ppb, and to 20 ppb at five hour intervals beginning at 8:00 on 28 September. The results for this calibration exercise are shown in panel c) of Figure 1-1. A thirteen hour period of scrubbed air was presented to instruments prior to the 5 ppb step – four of the six instruments reported values near 1 ppb, while the WEDD instruments were still recovering from the 40 ppb spike on the previous day. This roughly 1 ppb offset equates to uncertainties of up to 20%, 10%, and 5% for the delivered 5, 10, and 20 ppb concentrations in these tests. Again, with the exception of the Nitrolux system, all instruments recovered the calibration concentrations well, and the TDLAS and LOPAP showed the fastest time response. Once again the IMS reports concentrations about 20%

high, and the Nitrolux reports concentrations at least 25% low. The WEDD2 system failed beginning at 16:00 and was taken off-line.

Time response is clearly a major issue and does not allow for meaningful correlation analyses, as is typically done for intercomparisons. To compare instrument responses after responses have largely stabilized, Table 1-2 presents the root mean squared error (RMSE) for the six instruments calculated as the deviations from the calibration values used for the exercises shown in Figure 1-1. This table illustrates "best case" results, after the instruments have had relatively long periods of time to adjust to the delivered calibration values. Excluding the TDL result on 9/15 (for which the TDLAS used background correction), the LOPAP and TDLAS each have RMSEs of slightly less than 10%. The IMS and WEDD instruments have RSMEs very close to 20%, and the Nitrolux has an RMSE of 35%. The IMS and Nitrolux errors are caused by readings that are systematically high and low, respectively, and could be significantly improved with better factory an/or user calibrations.

Table 1-2. Root Mean Square Errors (RMSEs), calculated as deviations from calibration values, for calibration events listed. The error values are expressed as percent of the calibration value.

Date	Time	[NH_3]	TDL	IMS	Nitrolux	LOPAP	WEDD1	WEDD2
9/15	3:00-7:59	20 ppb	32%	14%	31%	13%	3%	24%
9/22	14:00-16:59	5 ppb	16%	23%	44%	10%	19%	15%
9/23	3:00-7:59	10 ppb	17%	22%	30%	11%	33%	9%
9/28	11:00-12:59	5 ppb	9%	22%	48%	7%	33%	27%
9/28	16:00-17:59	10 ppb	3%	23%	32%	4%	9%	31%
9/28	22:00-23:59	20 ppb	3%	20%	24%	4%	22%	N/A
AVERAGE NORMALIZED ERRORS			13%	21%	35%	8%	20%	21%

1.3.2 Spike Tests

In addition to the "negative" spike from the first calibration exercise shown in Figure 1-1a), two 40 ppb spike exercises were performed. The first exercise, illustrated in Figure 1-2a), followed an overnight period of zero air with a one hour period of 40 ppb calibration gas. Again it is clear that the TDLAS is the fastest responding of the instruments. The response time of the TDLAS is the upper limit of the response time of the manifold and calibration system, and other measurements of TDLAS response time indicate that the measured response time for the TDLAS is dominated by (and therefore very close to) the response time of the manifold and calibration system (23). There are some missing data points for the TDLAS, but figure 1-2 a) shows that it is the only instrument that reports a stable concentration for more than a few minutes of the hour long 40 ppb period. The LOPAP is the next instrument to respond, followed by the IMS. These two instruments report concentrations approaching 40 ppb and clearly show that the NH_3 concentration was a sharp spike. The Nitrolux and WEDD systems had a great deal of difficulty tracking the rapid change in NH_3 concentration in this and the following spike test. There must be very different mechanisms responsible for the significant degradation of response time for the two systems, since the Nitrolux samples and detects NH_3 only, while the WEDD systems rapidly dissolve NH_3 into a water stream, then measure the resulting NH_4^+ ion. The cause of the slow response of the WEDD system has yet to be resolved and is in contrast to the response to application of a liquid standard (in place of the diffusion scrubber) for which 95% response is achieved within 20 minutes.

The second hour long 40 ppb spike was preceded by three hours of 5 ppb calibration mixture and followed by four hours of the same. This was done in recognition of the possibility that the factors contributing to delays in instrument response may be different when starting from 5 ppb “background” than they are when starting from “zero.” Figure 1-2 b) seems to show that there is a difference in response for at least four of the five measurement systems.

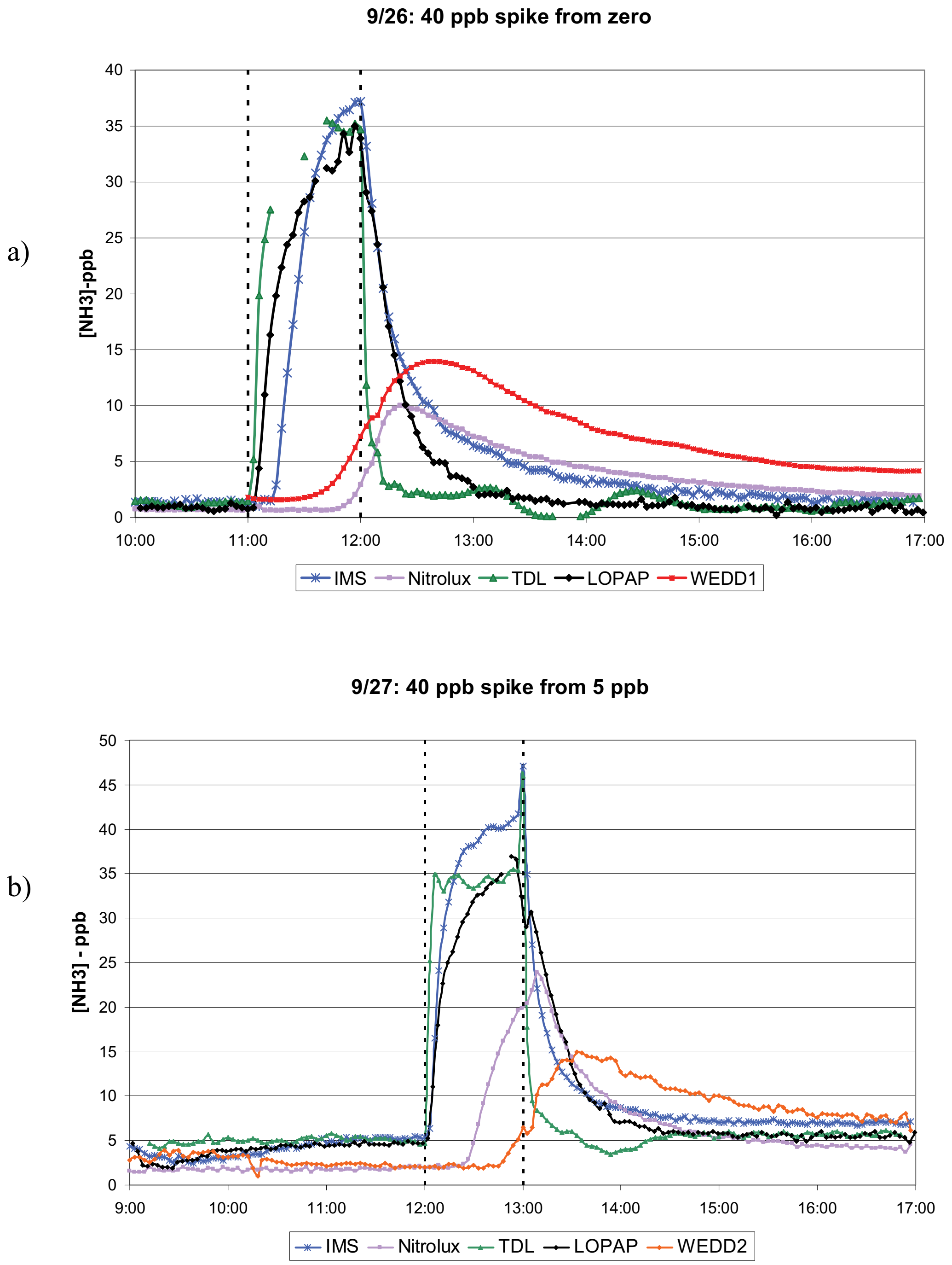

Figure 1-2. Instrument responses to two 40 ppb spike calibrations. a) [NH_3] is increased from zero to 40 ppb for one hour, then back to zero. b) [NH_3] is increased from 5 ppb to 40 ppb for one hour, then back to 5 ppb.

The TDLAS reaches a value near 35 ppb within six minutes and stays near there for more than 50 minutes until the NH_3 concentration is adjusted from 40 ppb to 5 ppb. At that point the TDLAS and IMS report transient spikes before falling off, with the TDLAS falloff occurring more rapidly than the other instruments. While the LOPAP responded more rapidly in the first 40 ppb spike test, the IMS and LOPAP rise times are virtually identical in this case, and the IMS fall time may be a little faster. The Nitrolux rise time may be a little faster for this test, but the biggest difference is the magnitude of the response – a maximum response of 25 ppb for the second test compared to a maximum response of 10 ppb for the first test.

1.3.3 Ambient Sampling

Manifold concentrations cannot be assumed to reflect true ambient gaseous NH_3 concentrations during ambient sampling, since the manifold was heated to near 40º C and volatile ammonium aerosols may have decomposed and contributed to the ambient gaseous NH_3 concentrations, nevertheless these data reveal information regarding instrument performance. There were two notable excursions or spikes in the manifold NH_3 concentrations that are shown in Figure 1-3. There are no TDLAS data for the period shown in Figure 1-3 a) because the Wintel software was unable to lock the laser line as required for a valid measurement. In this event, the NH_3 concentration jumped from a consensus value of 2-3 ppb to a higher value of 5-7 ppb over the course of an hour or less (based on the rise in LOPAP data), then slowly decreased over the next four to eight hours. All instruments show the rise and fall, but as with the calibration exercises, there are systematic differences in the timing and magnitude of the responses. The LOPAP has the fastest rise and fall times for this event, and the maximum value of more than 7 ppb agrees reasonably well with the IMS maximum of about 8 ppb. The IMS rise time is noticeably slower than the LOPAP's, and its fall time is much slower. The two WEDD instruments agree very well for this event, but their maximum values of around 5 ppb are much lower than those for the LOPAP and IMS. The timing of the peak concentrations is similar for the IMS and WEDD instruments. The Nitrolux data show a much slower response and a much lower peak concentration of about 3 ppb.

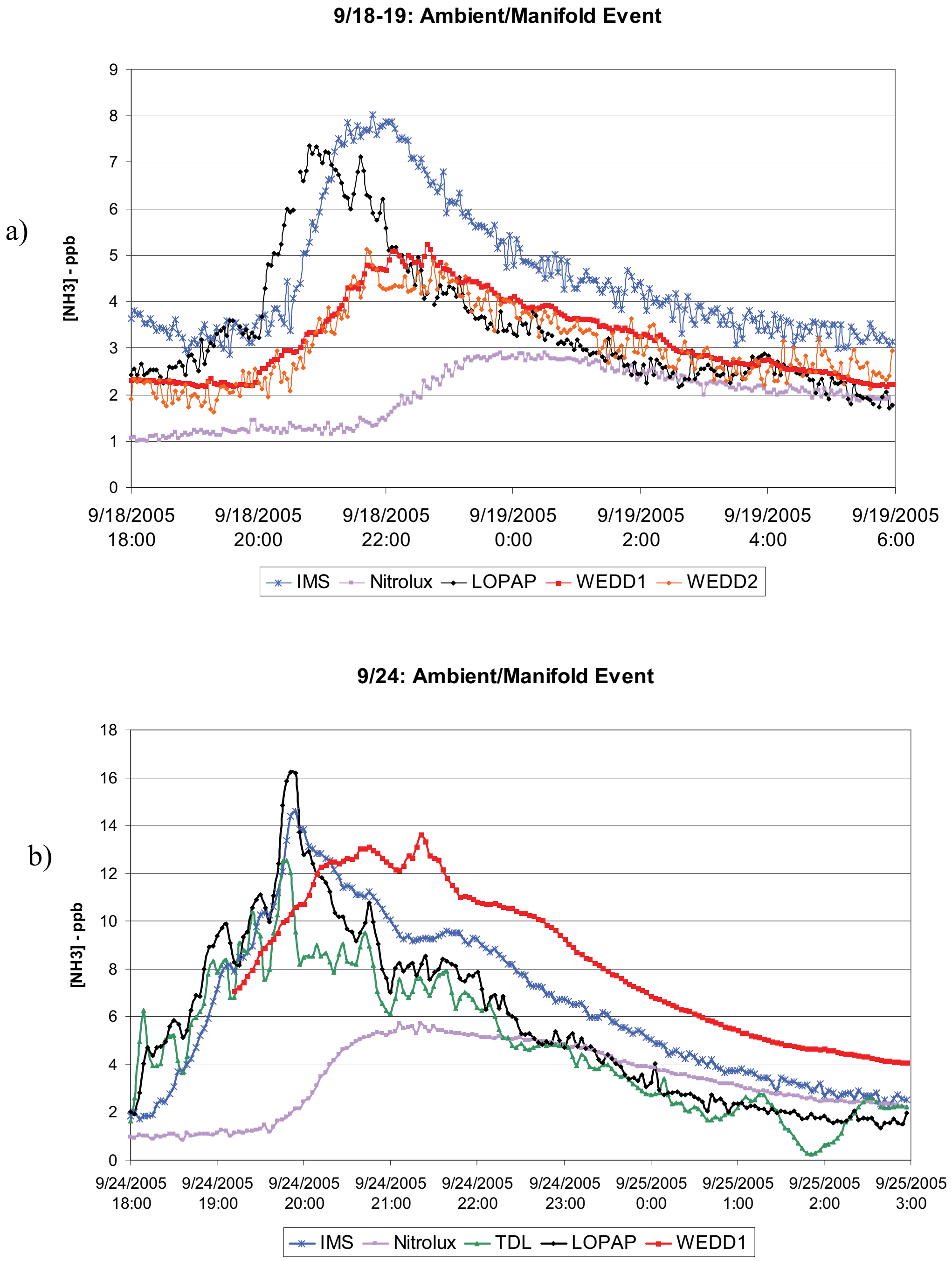

Figure 1-3. Instrument responses to ambient air sampled through the heated sample manifold for two periods are shown. a) Data from September 18 and 19, 2005. b) Data from September 24 and 25, 2005.

For the second ambient/manifold event, shown in Figure 1-3b) the TDLAS was operational and much higher NH_3 concentrations were encountered. The TDLAS and LOPAP data in particular also show evidence of significant concentration variability on the three minute common time scale. The TDLAS, LOPAP, WEDD, and IMS instruments all report maximum NH_3 concentrations between 12.5 and 16.2 ppb for this event. The WEDD instrument reaches this peak about an hour later than these other three instruments, and falls off the slowest, followed by the IMS. Once again the Nitrolux derived concentrations are biased low, reporting a peak value of less than 6 ppb.

1.3.4 Time Response

Instrument response time has been shown to be an important characteristic for the tested systems. To further quantify these observations, we have determined a set of response times for the instruments as they react to step changes in NH_3 concentrations supplied to the manifold. For each of these step changes presented below, we determine the time for each instrument to reflect 10%, 50%, 90%, and 95% of the change in concentration as measured by that instrument. Thus T10, T50, T90, or T95 is the time in minutes from the point when the manifold concentration is changed until the instrument response equals the 10%, 50%, 90%, or 95% concentration change.

Table 1-3 a) and Figure 1-4 a) illustrate the rise times for a zero to 20 ppb calibration exercise. As has been noted above, the TDLAS responds faster than any other technique, followed by the LOPAP and IMS methods. The WEDD system and the Nitrolux take much longer to begin responding to the step change and to reach the 90 and 95% change values. Table 1-3 b) and c) and Figure 1-4 b) and c) show the response times (both rise times and fall times) for the 40 ppb spike tests. Since the 40 ppb NH_3 calibration air was reduced to 0 or 5 ppb after only an hour for these tests, the longer fall times make sense in the context of typical response times approaching or exceeding an hour for all instruments except the TDLAS. That is, if the NH_3 is shut off (or drastically reduced) while the instrument is still approaching equilibrium with the 40 ppb NH_3 level, the “fall time” actually consists of the residual rise time plus the fall time.

a)

Instrument	Rise Times – 0 – 20 ppb step			
	T10	T50	T90	T95
TDL	9	17	60	78
LOPAP	18	32	128	164
IMS	42	60	135	150
WEDD1	87	156	267	288
WEDD2	75	132	260	280
Nitrolux	99	135	213	237

b)

Instrument	Rise Times – 0 – 40 ppb step				Fall Times – 40 – 0 ppb step			
	T10	T50	T90	T95	T10	T50	T90	T95
TDL	3	6	18	36	1	2	9	12
LOPAP	5	11	35	48	2	13	38	55
IMS	16	26	42	48	3	14	77	120
WEDD1	44	60	81	85	63	111	216	240
WEDD2	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Nitrolux	54	67	75	78	36	81	213	255

c)

Instrument	Rise Times – 5 – 40 ppb step				Fall Times – 40 – 5 ppb step			
	T10	T50	T90	T95	T10	T50	T90	T95
TDL	1	2	3	5	1	3	14	33
LOPAP	4	10	38	47	2	17	47	55
IMS	4	9	24	36	2	9	36	51
WEDD1	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
WEDD2	51	68	84	92	46	84	162	180
Nitrolux	30	42	76	78	15	30	97	125

Table 1-3. Instrument response times in minutes to step changes in concentrations.

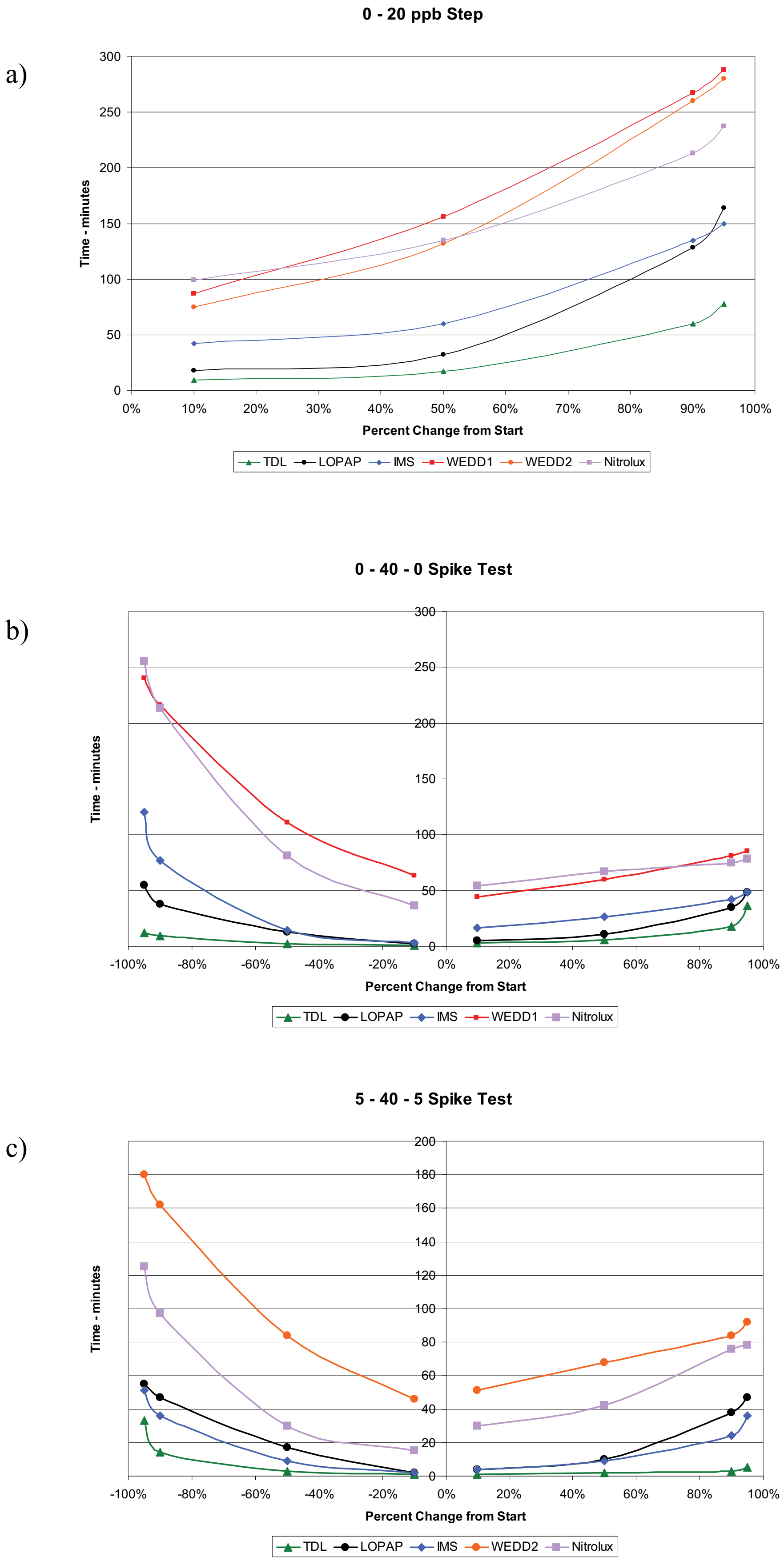

Figure 1-4. Instrument response times to step changes in the ammonia concentrations supplied by the calibration system. a) A zero to 20 ppb step performed as part of a calibration exercise on 9/19/2005. b) Rise and fall times for the zero to 40 ppb and 40 to zero ppb steps that made up the September 26 spike test. c) Rise and fall times for the 5 to 40 ppb and 40 to 5 ppb steps that made up the September 27 spike test.

A number of issues need to be addressed in the context of understanding the instrument time responses. First, the time response of the calibration system and sampling manifold to step changes in NH_3 concentration could seriously confound or compromise any analysis of instrument response times. The spike test illustrated in Figure 2 b) indicates that the TDLAS responds in a manner of minutes up to the 95% level. This means that the calibration system responds at least that quickly – at least for that test. That is, the TDLAS response time is an upper limit to the calibration system/manifold response time. Second, these response times generally present a worst case scenario for real-world conditions. We believe that the long instrument response times reflect the time required for gaseous NH_3 (or aqueous ammonium for the WEDD or LOPAP systems) to establish equilibrium with the surfaces of fluid handing tubes and components. These surface interactions come to equilibrium differently depending on their recent histories, as illustrated in Tables 3 b) and 2 c) and Figures 4 b) and 4 c). The longest response times are determined for cases for which zero air has run for many hours, effectively stripping off essentially all the NH_3 (or NH_4^+) stuck to the surfaces of the fluid handling components.

For these reasons, the time response numbers reported here in Table 3 and Figure 4 should be considered in the controlled context in which they were measured. That is, true ambient concentrations typically will not change from 0 to 40 ppb in the space of a minute or two (except near sources), and the instruments will have a little more time to respond to changing concentrations. That being said, it is clear from Figure 3 that different instruments used in this intercomparison report different peak values and timing of peak values for the ambient spikes measured during the ambient/manifold sampling periods, and response times will have an effect on timing and peak concentrations of ambient measurements in many situations.

1.4 CONCLUSIONS – LABORATORY INTERCOMPARISON

With the exception of the modified chemiluminescence analyzer, the instruments performed well, and under stable calibration conditions, generally agreed to within about 25% of the expected calibration value. Instrument time response is shown to be sensitive to measurement history as well as sample handling materials and is shortest for the TDL.

The IMS and Nitrolux are commercial instruments used without modification from the manufacturer. These two instruments have significantly slower time response than the TDLAS, (especially in the case of the Nitrolux), and exhibited measurement biases of approximately +25% (IMS) and -25% (Nitrolux). The LOPAP and WEDD instruments, both research instruments using wet chemical methods, performed well in the calibration tests in terms of the accuracy of measured concentrations, but the WEDD instrument suffered from significantly slower time response than the LOPAP.

Response time issues with ammonia measurement systems make evaluations and intercomparisons particularly difficult. The Nitrolux, and at times the IMS and WEDD instruments, had unacceptably long time responses in these experiments. The varying time delays also precluded doing meaningful correlations of the data sets. Instrument responses to stable concentration values were mostly within 25%. The TDLAS and LOPAP reported values closest to the delivered concentration values. While the WEDD instruments had larger errors, the IMS was biased 21% high and the Nitrolux was biased 35% low. Sub-ppb measurement of gaseous ammonia is possible with current research and commercial instruments, but time response and accuracy are issues that need to be addressed very carefully to obtain quality assured data.

2 CONTINUOUS MEASUREMENTS OF AMMONIA AND NITRIC ACID AT A RURAL NEW YORK SITE

2.1 INTRODUCTION – FIELD MEASUREMENTS AND EVALUATION

Ammonia and nitric acid are trace gases that are not routinely monitored at atmospheric chemistry and air quality measurement sites, but are of great interest to scientists and policy makers as they try to understand the air quality problems of oxidant and particulate matter formation. The EPA NCORE program strategy lists both nitric acid and ammonia as target species for continuous measurement, but there are not yet recommended continuous methods for either species (EPA 2005). Measurement methods for these species have been proposed, deployed, and intercompared many times in the past twenty years (Hering et al. 1988; Sickles et al. 1990; Williams et al. 1992; Fehsenfeld et al. 2002). As shown by the intercomparisons, and by a handful of more recent studies, the methods that exhibit the greatest accuracy, precision, and stability tend to be research methods like Chemical Ionization Mass Spectrometry (CIMS) (Fehsesnfeld et al. 1998); Tunable Diode Laser Absorption Spectrometry (TDLAS) (Li et al. 2006); and Liquid Scrubbing followed by detection using HPLC, fluorimetry, or optical absorption (Pryor et al. 2001; Huang et al. 2002).

The drawback inherent in these powerful techniques is their resource requirements, both in terms of initial outlay and in terms of highly skilled labor. In this study we report on the deployment and operation of instrumentation for measuring nitric acid and ammonia that can be operated continuously and year round with relatively modest investments in equipment and labor. Data for a three month period in late winter and spring of 2006 is presented and discussed.

2.2 EXPERIMENTAL METHODS - FIELD MEASUREMENTS AND EVALUATION

2.2.1 Measurement Site

The Addison site is located in southwest New York State within the boundaries of Pinnacle State Park at an elevation of approximately 504 m above sea level. Its coordinates are 42.09° N and 77.21° W. It is located on the eastern slope of Orr Hill, part of the Allegany Plateau of southern New York State and northern Pennsylvania. Orr Hill rises steeply from the Canisteo River Valley and the village of Addison. Immediately adjacent to the measurement site to the north and west is a nine-hole golf course operated as part of the State Park. Adjacent to the park on the east and north are undeveloped State Forest lands. The surrounding area is a patchwork of vegetation types, including the golf course, mixed deciduous and coniferous forests, some former pastures and fields, and an approximately 50 acre pond to the south and below the site. The village of Addison (pop. ~1800) is 4 km to the northwest, and the town of Corning (pop. ~12,000) is 15 km to the northeast. The average annual temperature at the site is 7.8ºC; and the average range is from -18 to 31ºC.

2.2.2 Nitric Acid Measurement Method

We use a model 42S chemiluminescence instrument to measure HNO_3 by denuder difference in conjunction with NO_Y. The method involves using the switching technique of the commercial $NO/NO_2/NO_X$ analyzer – but instead of "NO" and "NO_X" measurement modes, the modified instrument uses "NO_Y-HNO_3" and "NO_Y" measurement modes. The "NO_Y-HNO_3" mode involves passing the sample through a chemically coated annular denuder and a heated molybdenum converter before it enters the analyzer's reaction and detection chamber.

The denuder difference method relies on the selective removal of the target species (in this case HNO_3) in one NO_Y-like measurement channel, while another channel – identical except for the denuder – measures "true" NO_Y. The difference between these channels is the HNO_3. Based on information from the EPA Compendium of Methods (EPA 1999), sodium carbonate was initially selected as the active chemical for nitric acid removal in

2000. Sodium carbonate was effective in chemically removing HNO_3 in the gas steam, but in early to mid-2002 we discovered that the Na_2CO_3 denuder captured not only the HNO_3, but also roughly 15% of the NO_2. An uncoated denuder was used for about a year from October of 2002 to September of 2003, but it was also unsatisfactory. Finally, in October of 2003, a denuder coating of 1% sodium chloride was tried. This appears to be the optimum chemical coating material for selective removal of HNO_3 and has been used ever since. Analog signals from the analyzer are averaged with a one minute base period and transferred automatically to a computer for storage.

2.2.3 Ammonia Measurement Method

While the original plan called for field deployment of one or more chemiluminesce based ammonia analyzers, the problems with this method presented above caused us to alter the field deployment plan. The ammonia analyzer chosen for deployment was the AirSentry Ion Mobility Spectrometer (IMS) purchased from Particle Measuring Systems (Boulder, CO). The technique uses ionization of the NH_3 molecule followed by electrostatic extraction of its ions into a drift chamber and detection at a collector plate. The shutter grid producing the extraction field is pulsed periodically to allow ions into the drift tube; and ion time-of-flight is used to identify the ammonia ion. Confirmation of the ion identification and quantification is obtained through the measured addition of a dopant molecule (in this case dimethyl methylphosphanate – $(CH_3)_3PO_3$).

Ambient air is sampled at ≈2.5 l/min through a heated, silica-coated 4.8 mm I.D. (1/4" nominal O.D.) stainless steel inlet line. In addition, a supply of clean, dry air (dew point below -40°C, flow rate less than 5 l/min) at a delivery pressure of 20-120 psig must be supplied to the analyzer. This instrument air flows into the IMS analyzer cell on one side of a semi-permeable membrane, and the ambient air sample flows into the cell on the other side of the membrane. NH_3 in ambient air passes through the membrane and is picked up by purified instrument air, which delivers it to the reaction region. Low-level beta energy from a sealed nickel-63 radiation source ionizes the sample air. These ions are drawn out of the reaction region and flow counter to the drift gas flow. During this counter flow period the ions separate in time based on their chemical and physical properties before being detected by a Faraday plate detector at the end of the drift tube. Detection selectivity is achieved through specificity of the semi-permeable membrane and through the consistent time-of-flight of the ammonia ions as they traverse the stable drift flow. Zero response and calibration checks are performed from the front channel keypad. (Note that calibration checks require the optional add-on permeation source.)

The AirSentry uses eight individual time-of-flight spectra to produce each sample concentration, which equates to an averaging period of less than 0.2 seconds. Samples may be further averaged using a user-selectable smoothing factor (we used a smoothing factor of 250 for the field measurements), which calculates a rolling average concentration value. These values are transferred as a serial string to a computer and recorded once a minute.

2.3 RESULTS - FIELD MEASUREMENTS AND EVALUATION

2.3.1 Measurements of ammonia and nitric acid

One-hour averaged data was calculated using the valid minute averaged data points. We required at least 30 valid minute averages to obtain a valid hour average data value. A time series of the measured nitric acid and ammonia concentrations from February 24 to May 31, 2006 is shown in Figure 2-1. The numerous breaks in the ammonia time series are due mainly to calibration periods and the rather long period required for the ammonia from the calibration source to fall to background levels. The scale for these two species is quite similar, ranging from close to zero to slightly less than six ppb. It appears at first glance that the HNO_3 and NH_3 peaks may coincide (Julian days 89, 100, 149, 150), but the data is not well correlated at all. Table 2-1 presents the summary statistics for ammonia and nitric acid during the measurement period.

	NH_3	HNO_3
Mean	1.06 ppb	0.66 ppb
Standard Dev.	0.77 ppb	0.62 ppb
Median	0.87 ppb	0.48 ppb
Maximum	5.82 ppb	5.75 ppb
Est. MDL	0.3 ppb	0.2 ppb
Completeness	90.1%	85.4%

Table 2-1. Summary statistics for the measurement of ammonia and nitric acid at Pinnacle State Park during March – May 2006.

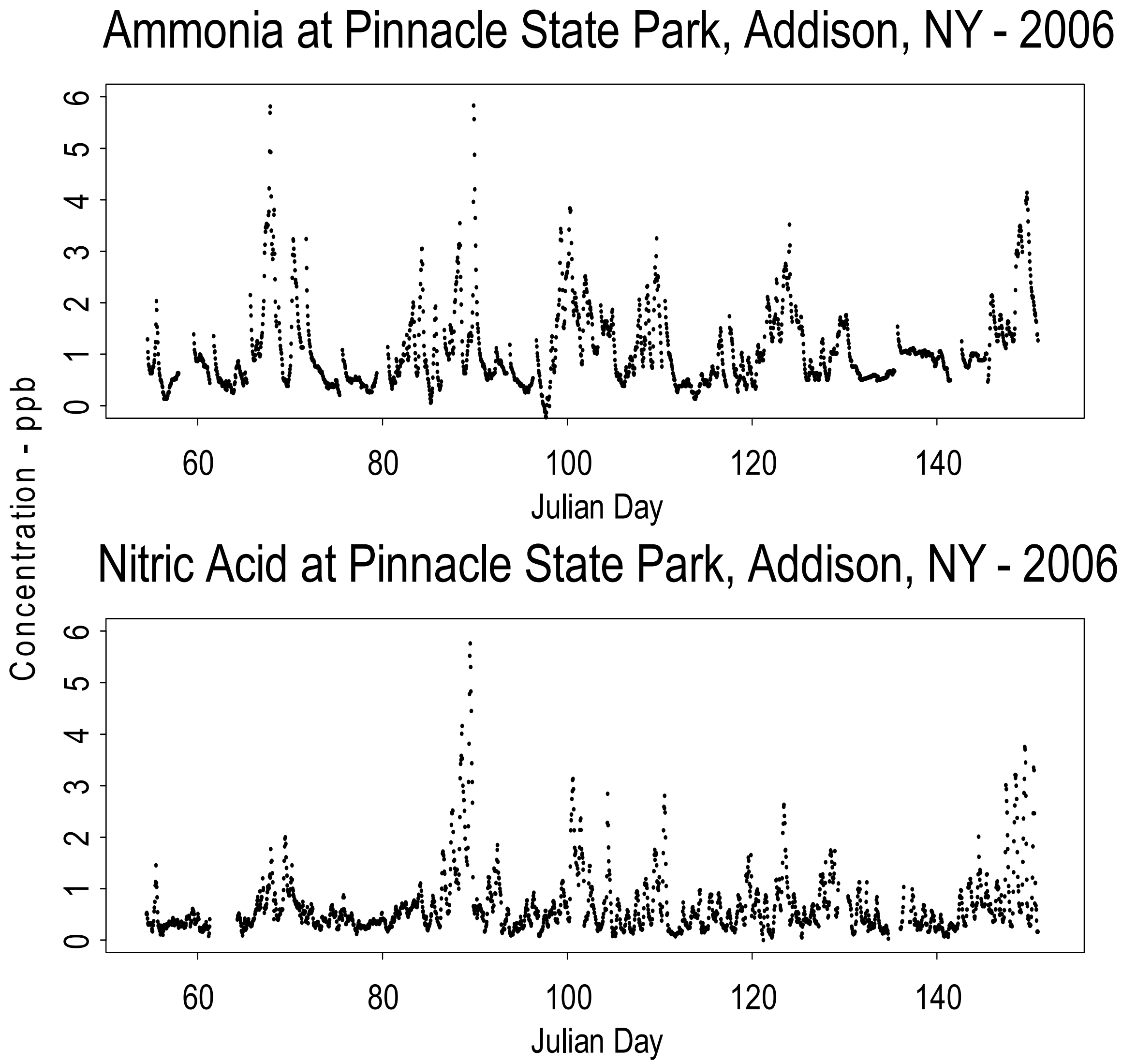

Figure 2-1. Ammonia and nitric acid time series.

To illustrate the interrelation between ammonia and nitric acid, two time periods are examined in more detail. The first of these periods is Julian days 85 to 90 (March 27 to April 1, 2006). Both species plotted together are shown in Figure 2-2. While concentrations of both gases reach their highest values in the study during this period, they do not reach high values at the same time. For the most part, ammonia is only high when nitric acid is low, and vice versa. This is not surprising – even though it is somewhat surprising that they reach relatively high levels only a few hours apart. A more detailed analysis including data from other pollutants and meteorological parameters – especially temperature and wind direction – should help our understanding of these data.

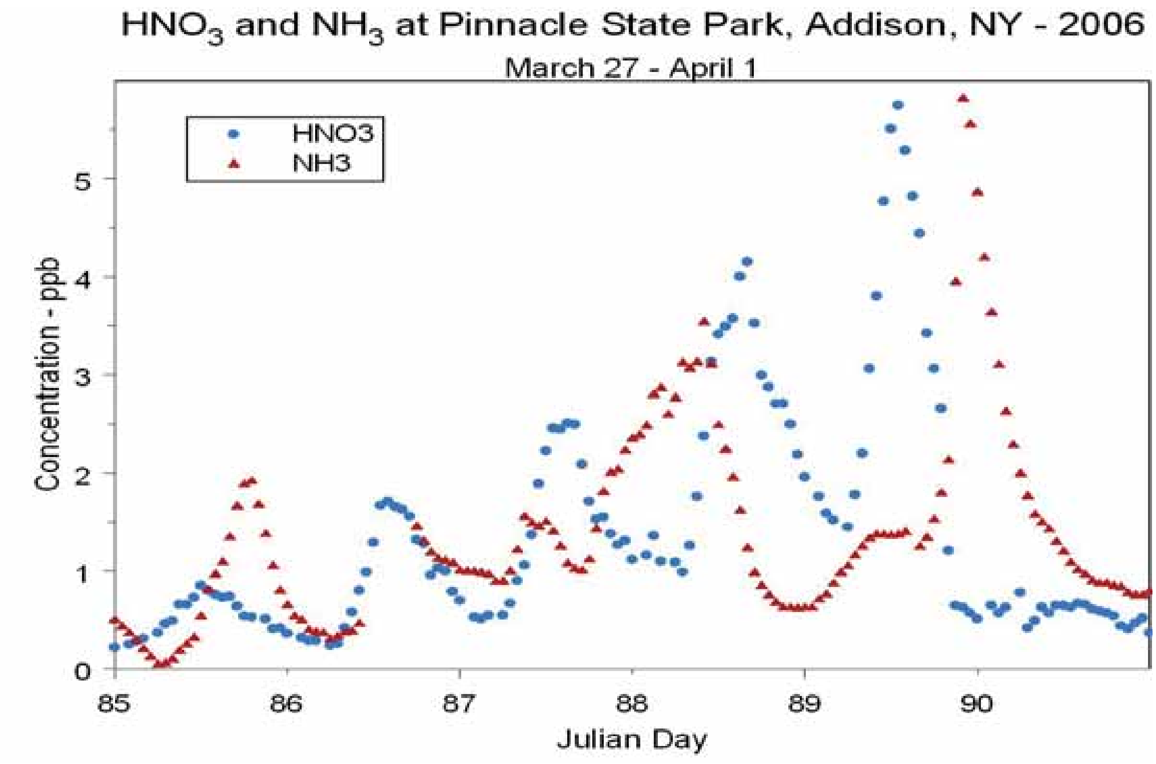

Figure 2-2. Ammonia and nitric acid for the period March 27 – April 1, 2006.

A second period of interest is the end of May, shown in Figure 2-3. This was at the very end of the study period, and nitric acid exhibits a very strong diurnal behavior over the last four days – dropping well below one ppb at night and increasing to over three ppb each day. Ammonia also shows daily peaks, but the peaks are in the late evening or night, after the nitric acid daily maxima. The reported ammonia concentrations do not decrease to low minimum levels like the nitric acid – a phenomenon that may be due more to measurement problems than to true atmospheric concentrations. Further work needs to be done to confirm the ability of the sampling lines and the instrument itself to follow rapidly changing concentrations under all atmospheric conditions.

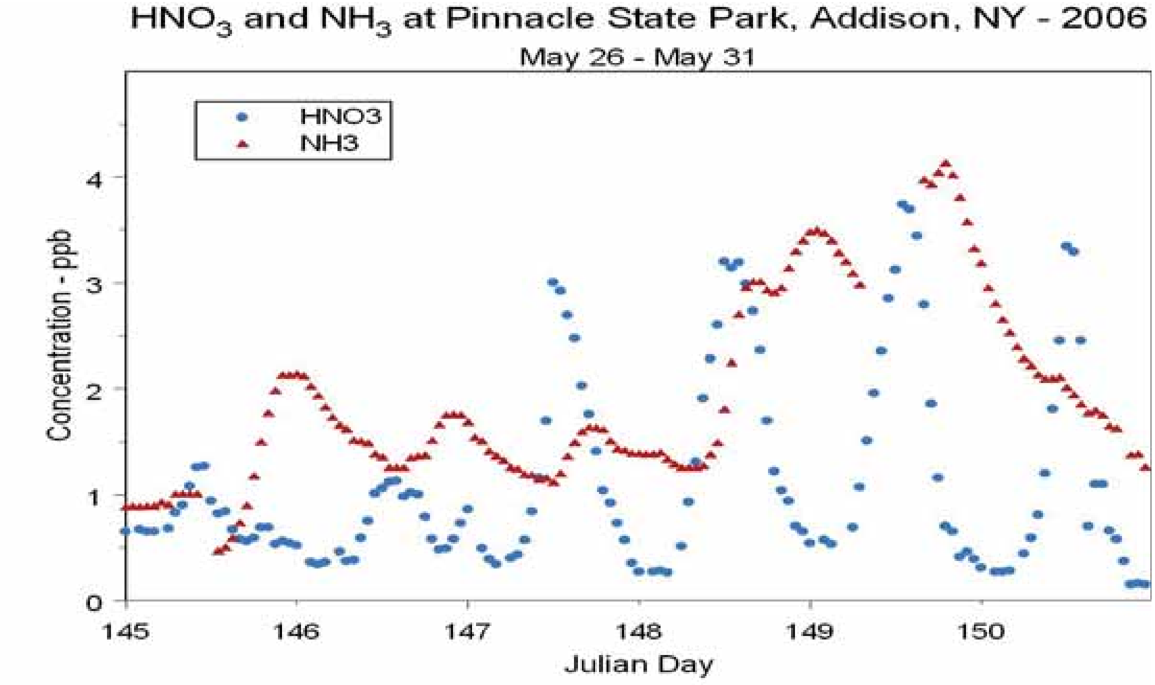

Figure 2-3. Ammonia and nitric acid for the period May 26 – May 31, 2006.

2.3.2 PM nitrate formation

With continuous measurements of ammonia, nitric acid, temperature, and relative humidity, we can empirically explore the equilibrium between gaseous ammonia and nitric acid, and particle phase ammonium nitrate. In particular, we can determine the "tendency" of the gaseous precursors to condense into ammonium nitrate. The analysis presented here is only a rough estimate because other gaseous and aerosol phase components will affect the equilibrium; and perhaps more importantly, production and losses of the gaseous and aerosol species are not well accounted for in a simple model that considers only equilibrium chemistry. With this limitation in mind, it is still quite useful to use the measured data to gain insight into the tendency for ammonium nitrate formation.

The equilibrium constant for particle phase nitrate formation depends strongly on relative humidity and temperature (Seinfeld and Pandis 2006). The relative humidity dependence is discontinuous; that is, below the deliquescence relative humidity (DRH, roughly 62 – 77 % for typical ambient temperatures at PSP) there is no dependence of the equilibrium constant on RH, while above the DRH, the equilibrium constant decreases rapidly with RH, shifting the equilibrium strongly toward the aerosol phase. For simplicity, we will only calculate the equilibrium constant for humidities below the DRH, bearing in mind that above the DRH, the tendency to form aerosol nitrate will be greater. The temperature dependence of the equilibrium constant (K_p) can be quite nicely estimated by integrating the van't Hoff equation, resulting in equation 2-1:

$$\ln K_p = 84.6 - \frac{24220}{T} - 6.1 \ln\left(\frac{T}{298}\right) \qquad (2-1)$$

Using the measured data, the temperature data is first used to calculate the DRH. This is done to determine if the simple equilibrium constant shown as Equation 2-1 is applicable. The temperature is next used to calculate K_p for the simple case (i.e., RH < DRH). Next, the product of gaseous ammonia and nitric acid concentrations $[NH_3]*[HNO_3]$ is calculated from the data. Hour-averaged data is used for the calculation, although minute-averaged data could be used in principle, and may show additional detail.

Figure 2-4 shows results from the EPA Speciation Trends Network (STN) protocol 24-hour integrated filter measurements collected at PSP every third day. These are the only measurements of aerosol nitrate we have for this site, and they are clearly limited due to the 1-in-3 day collection schedule and the long time averaging. Still, inspection of Figure 2-4 clearly indicates that aerosol nitrate is highest on March 9, March 24, and March 30; these dates might be best candidates for further study. Based on this, we have examined the nitrate equilibrium for two periods: March 9-10 and March 30 – April 1. As indicated above, the first consideration is the effect of relative humidity. We define the quantity "RRH" as a ratio of relative humidities, namely the ratio of the ambient relative humidity to the deliquescence relative humidity for ammonium nitrate. Following the discussion above, when RRH is less than 1, ammonium nitrate exists as a solid and the equilibrium constant is calculated simply from Equation 2-1. However, when RRH is greater than 1, ammonium nitrate is “in solution”, and the equilibrium is shifted to aerosol phase by as much as a factor of 10. Whenever the “equilibrium product” ($[NH_3]*[HNO_3]$) is greater than K_p, the equilibrium favors formation of aerosol nitrate.

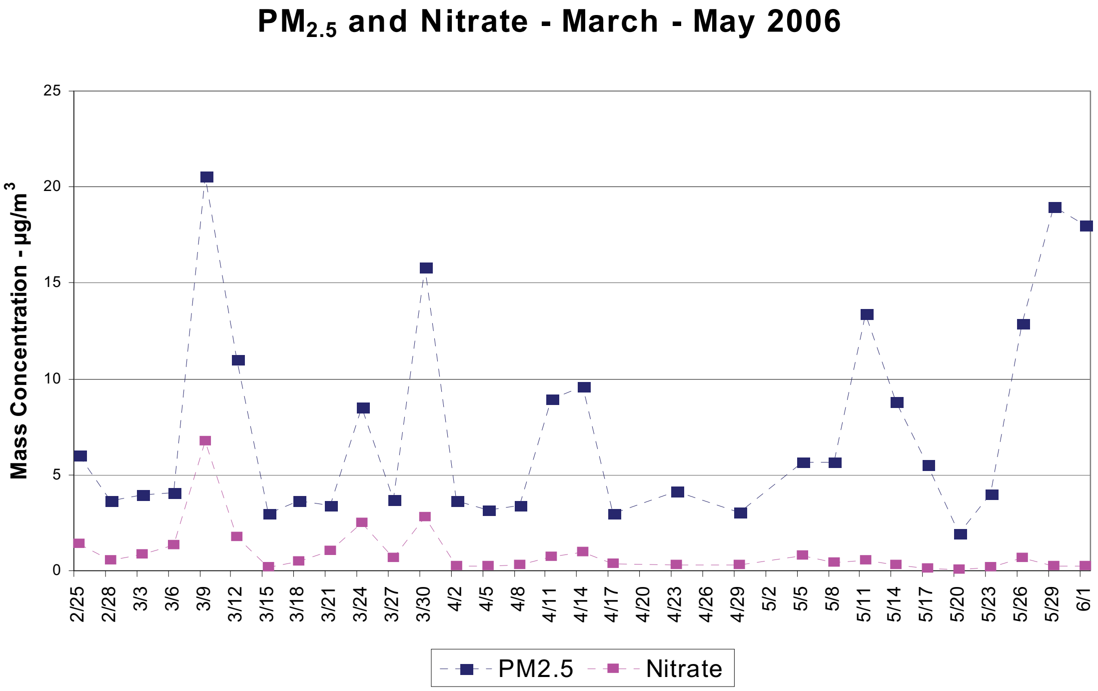
$PM_{2.5}$ and Nitrate - March - May 2006

Figure 2-4. $PM_{2.5}$ total mass concentration, and nitrate mass concentration form the Speciation Trends Network (STN) 24-hour filters collected every third day at PSP.

Figures 2-5 and 2-6 show the equilibrium tendencies for the periods March 9-10 and March 30 – April 1. Plotted in each figure are the ratio of relative humidities (RRH), the equilibrium constant for RH < RRH (K_p), and the equilibrium product $[NH_3]*[HNO_3]$ (prod). The main trend to focus on in these figures is the difference between “prod” (the equilibrium product) and “K_p” (the equilibrium constant). In Figure 2.5 there is a large difference between these two quantities throughout the day on March 9, with a maximum difference at the end of the day. There is a clear tendency toward aerosol nitrate formation from this analysis, which is consistent with the large aerosol nitrate measurement on March 9 by the STN filter shown in Figure 2-4. Figure 2-6 shows a large difference between “prod” and “K_p” on March 30, in this case maximizing around midday. In fact, K_p and prod are roughly equal by the end of the day on March 30, so the tendency to produce aerosol falls dramatically by that point.

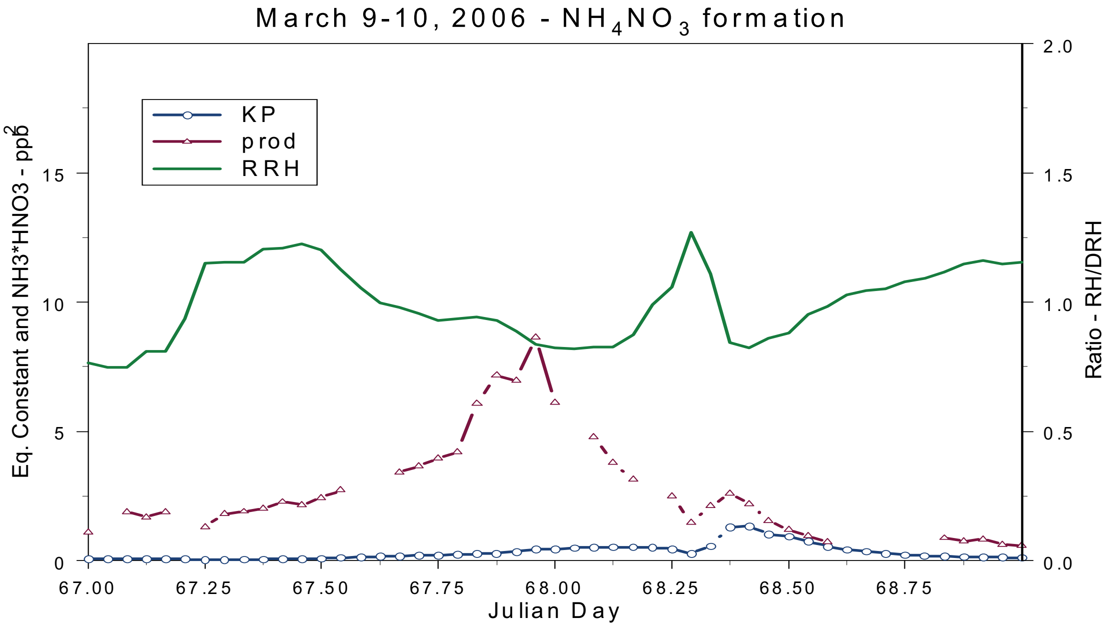

Figure 2-5. Exploration of the tendency to produce aerosol nitrate for March 9 – 10 at PSP. See text for explanation of the quantities plotted.

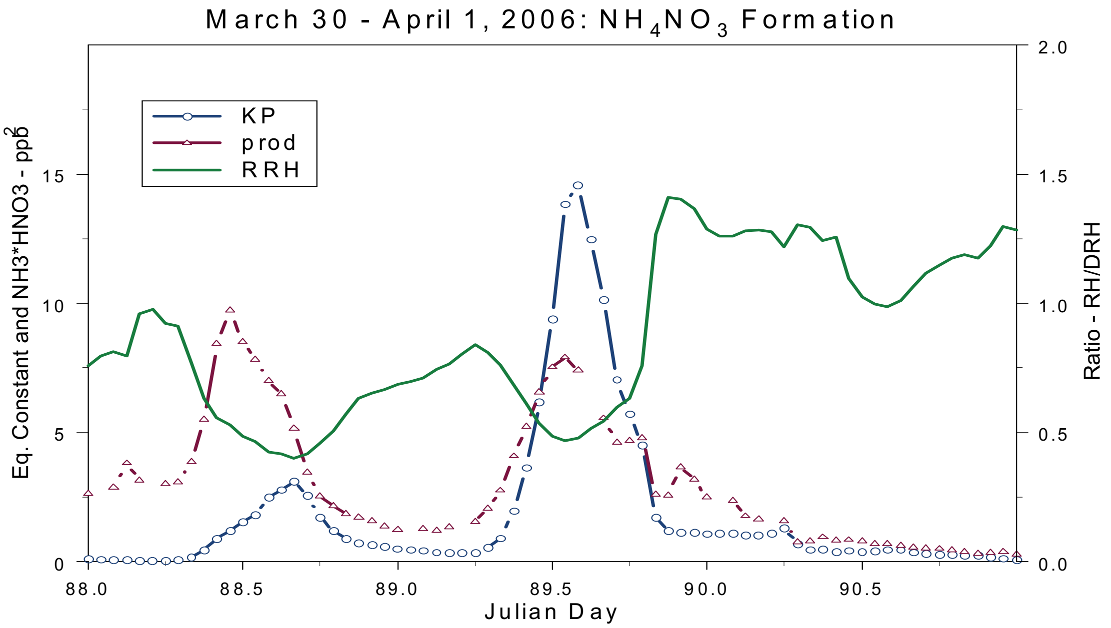

Figure 2-6. Exploration of the tendency to produce aerosol nitrate for March 30 – April 1 at PSP. See text for explanation of the quantities plotted.

On March 9, the STN filter sample reported a 24-hour average nitrate concentration of 6.73 µg m^{-3}. The measurements of gaseous ammonia and nitric acid for that day show that $[HNO_3] < [NH_3]$, so production of aerosol nitrate is limited by the supply of nitric acid. If all the measured nitric acid is assumed to produce aerosol ammonium nitrate each hour, the corresponding average production rate of "nitrate" is 3.24 µg m^{-3} hr^{-1}. For March 30 (shown in Figure 2-2) the ammonia concentration is larger early in the day, and the nitric acid concentration is larger later in the day. If we again fully convert the limiting reagent to aerosol nitrate each hour, the calculated average production rate is 4.62 µg m^{-3} hr^{-1}. The STN measurement reported an average nitrate concentration of 2.83 µg m^{-3} for the day. We believe these calculations give reasonable estimates of the tendency to produce ammonium nitrate aerosol, but they cannot be expected in and of themselves to explain the details of the rate of aerosol mass accumulation and instantaneous or average mass concentration. More detailed modeling that includes transport and losses of the gaseous and aerosol species would be required to obtain those quantities.

2.4 SUMMARY - FIELD MEASUREMENTS AND EVALUATION

Continuous low-level measurement of gaseous ammonia and nitric acid has been demonstrated for a three month period at a rural site in southwestern New York State. Nitric acid is measured by denuder difference and chemical conversion using heated molybdenum converters and chemiluminescence detection of nitric oxide (NO). Ammonia is measured with a commercial Ion Mobility Spectrometer (IMS). Both techniques provide adequate sensitivity to detect and quantify the sub-ppb levels of these species often encountered at the measurement site. Measurements show that nitric acid and ammonia are often elevated during the same overall time periods, but peak concentrations are always offset, such that maximum nitric acid occurs while ammonia is at a minimum (or decreasing), and vice versa. For this ammonia analyzer the issue of time response, and more specifically, the ability of the analyzer to accurately track rapid up and down changes in ammonia concentrations, requires further evaluation. Along with temperature and RH, one can easily determine the tendency to produce nitrate aerosol, but details of the rate of accumulation and expected mass concentrations require additional modeling.

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