

Nitric acid and ammonia at a rural northeastern U.S. site

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Abstract. Hourly mixing ratios of HNO₃, NH₃ and various other trace gas and aerosol species were determined at Harvard Forest in central Massachusetts between 1991 and 1995 in order (1) to ascertain the representativeness of this composite data set, (2) to identify general seasonal and diurnal trends in the mixing ratios of HNO₃ and NH₃ at this site, (3) to establish how these mixing ratios depend on characteristic meteorological parameters such as wind direction and temperature, and (4) to examine HNO₃ relative to the other reactive nitrogen species measured. Harvard Forest receives air masses from both urban and rural source regions resulting in mean midday HNO₃ mixing ratios 4 times higher when surface winds were from the SW (~ 2000 parts per trillion by volume (pptv)) as opposed to the NW (~ 500 pptv) wind sector. The HNO₃ diel cycle provides evidence of entrainment of HNO₃ from aloft as the nocturnal inversion breaks down. Gaseous NH₃ mixing ratios are typically 200-300 pptv and on average exhibit little diel variability. High levels of atmospheric sulfate consistently suppress NH₃ concentrations below the predicted NH₃ compensation point of the canopy, even during periods when the sum of NH₃ and NH₄⁺ (NH_x) mixing ratios are quite high. The aerosol SO₄²⁻ regulation of NH_x partitioning changes as a function of temperature. At the same SO₄²⁻ mixing ratio, colder ambient temperatures result in lower NH₃/NH_x. On average HNO₃ makes up about 20% of NO_y at midday. The sum of the measured NO_y species (NO, NO₂, HNO₃, and particulate NO₃) typically account for 60-80% of NO_y, suggesting that peroxyacetyl nitrate and other organic nitrates are a significant fraction of NO_y at this predominantly oak forested site.

1. Introduction

The family of odd nitrogen trace species known as NO_y (NO_y ≡ NO + NO₂ + NO₃ + N₂O₅ + nitric acid (HNO₃) + aerosol nitrate (NO₃⁻_(p)) + peroxyacetyl nitrate (PAN) + other organonitrates) is integral to the chemistry of the atmosphere. Besides regulating the rate of ozone (O₃) production and destruction reaction sequences, NO and NO₂ also affect tropospheric mixing ratios of hydroxyl (OH) and hydroperoxy (HO₂) radicals. By controlling these critical atmospheric oxidants, NO_x (NO + NO₂) is effectively involved in most atmospheric reaction cycles and the NO_x mixing ratio controls oxidative removal rates of many trace gases.

NO_x is directly emitted from combustion processes as NO but rapidly reacts with various oxidants (e.g., O₃, HO₂, organic peroxy radicals (RO₂)) to form NO₂. In the presence of sunlight, the photodissociation of NO₂ can regenerate NO in a matter of minutes, while slower reactions, occurring over a period of hours to days, may further oxidize NO₂ to nitric acid (HNO₃) or peroxyacetyl nitrate (PAN). At night, NO₂ can be oxidized (via O₃) to NO₃ or subsequently react with NO₃ to

form N₂O₅, that hydrolyses on aerosol surfaces to produce HNO₃ [Richards, 1983; Dentener and Crutzen, 1993].

The less reactive NO_y reservoir species (PAN and HNO₃) have different atmospheric fates. PAN is only stable at cold temperatures and essentially insoluble, and as such has the potential to be transported long distances in the cold upper troposphere. Thus delivered to remote regions, PAN can thermally decompose to NO_x in subsiding air. Although HNO₃ can react with various gases and particles (e.g., ammonia (NH₃) and soil/dust particles) to form nitrate containing aerosols, it is also very water soluble and readily adsorbs onto surfaces. Due to the large deposition velocity of HNO₃ it is efficiently removed from the atmosphere via both wet and dry deposition processes over short transport distances. Given the slow removal mechanisms of the other NO_y components, the removal of HNO₃ is the primary atmospheric NO_y sink.

Further interest in the fate of HNO₃ has been linked to the "fertilization" of N-limited ecosystems by atmospheric deposition [Schindler and Bayley, 1993]. As anthropogenic emissions of NO have steadily increased over the past several decades [Gschwandtner et al., 1986], so has the deposition of atmospheric nitrogen [Schell, 1987], thereby potentially inducing some systems to incorporate even more atmospheric CO₂ [Peterson and Melillo, 1985]. These investigations have highlighted the shortage of information regarding boundary layer HNO₃ mixing ratios and deposition fluxes, largely due to the difficulty in obtaining reliable ambient measurements. Even more scarce, and probably more difficult to acquire, are

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accurate measurements of gaseous NH₃ [Williams *et al.*, 1992], another potentially important source of N to the biosphere.

In addition to being an important nutrient for plant growth, NH₃ is the only gaseous base found in significant quantities in the atmosphere, and it is therefore fundamental in determining the overall acidity of cloudwater, precipitation, and atmospheric aerosols. Important sources of NH₃ include the decay of domestic livestock wastes, volatilization losses from fertilizers, biomass burning, and senescing vegetation [Schlesinger and Hartley, 1992]. Several studies indicate that growing vegetation can passively absorb or emit NH₃ directly through leaf stomata [Denmead *et al.*, 1976; Farquhar *et al.*, 1980; Langford and Fehsenfeld, 1992]. When ambient NH₃ mixing ratios are below a certain "compensation point," determined by the partial pressure of NH₃ within leaf stomata and perhaps the physiological state of the plant, NH₃ can escape to the atmosphere. The stomatal uptake of NH₃ is essentially the reverse process. Farquhar *et al.* [1980] noted that the compensation point of snap beans (*Phaseolus vulgaris*) was temperature dependent and could be described as the equilibrium NH₃ vapor pressure above an ammonium solution at a fixed pH of 6.8 (estimated to be the pH of the stomatal cell walls) and a NH₄⁺ concentration of 46 μM. Langford and Fehsenfeld [1992] observed a nearly identical relationship for the regulation of background NH₃ mixing ratios for air passing over the Roosevelt National Forest in Colorado and suggested that the NH₃ compensation point was a non-species specific mechanism perhaps related to photorespiration and assimilation.

Once NH₃ is released to the atmosphere, it has an average tropospheric lifetime of the order of hours to days before either (1) reacting with H₂SO₄ or HNO₃ to form a fine aerosol, (2) being scavenged by wet deposition, or (3) directly dry depositing to the Earth's surface. While NH₄⁺ may be involved in long-range transport if vertically advected into the free troposphere, NH₃ is typically deposited near its source.

Automated instruments to continuously measure atmospheric levels of NH₃ [Wyers *et al.*, 1993] and HNO₃ [Buhr *et al.*, 1995] have only recently been developed, consequently few long-term or high-resolution data sets exist for either species. The available longer term NH₃ measurements (weekly sample integration) indicate a seasonal cycle with summertime maxima and wintertime minima for the Harvard Forest in Petersham, Massachusetts [Tjepkema *et al.*, 1981]. Higher resolution (2 hour integration) summertime data show similar diurnal trends with nighttime minima and daytime maxima for NH₃ [Langford *et al.*, 1992]. It is thought the season and diel cycles of NH₃ arise from warmer temperatures leading to greater NH₃ emission rates.

Several years of weekly HNO₃ measurements reveal different trends for various regions of the United States. [Meyers *et al.*, 1991]. Variable HNO₃ seasonal trends may be a consequence of episodic HNO₃ events occurring throughout the year [Edgerton *et al.*, 1992]. The typical HNO₃ diel signal of higher values midday and lower levels at night [Parrish *et al.*, 1986] is thought to be a result of photochemical HNO₃ production and surface deposition [Kleinman *et al.*, 1994].

In the present study hourly measurements of HNO₃ and NH₃ have been obtained during 1991-1995 at a nonurban continental site for a wide range of meteorological conditions. Over the same period, NO, NO_x, NO_y and other important trace gas species and meteorological parameters were con-

tinuously measured [Munger *et al.*, 1996, 1998]. The purposes of this study were (1) to ascertain the representativeness of this composite data set, (2) to identify general seasonal and diurnal trends in the mixing ratios of HNO₃ and NH₃ at this site, (3) to establish how these mixing ratios depend on characteristic meteorological parameters such as wind direction and temperature, and (4) to examine HNO₃ relative to the other reactive nitrogen species measured.

2. Methods

2.1. Site Description and Ancillary Measurements

The Harvard Forest in Petersham (42°32' N, 72°11' W; elevation 340 m) is located in a wooded, rural area of central Massachusetts. The nearest large cities are Boston and Hartford, 100 km to the east and southwest, respectively. This 50-70 year old predominantly oak forest (mixed with maple, beech, birch, cherry, spruce, and pine) has an average canopy height of 23 m near the sampling site. Since the middle of 1990, the Harvard group has made continuous measurements of various atmospheric trace gases (NO, NO₂, NO_y, CO, CO₂, H₂O, O₃, and a suite of nonmethane hydrocarbons) from the top of a 30 m tower [Goldstein *et al.*, 1995; Goulden *et al.*, 1996; Munger *et al.*, 1996]. In addition, numerous micrometeorological and radiative properties (including wind speed, wind direction, temperature, relative humidity, photosynthetically active radiation, solar albedo, and net radiative flux) are continuously monitored by a variety of instruments collaboratively operated by both Harvard and the State University of New York at Albany [Moore *et al.*, 1996]. The fast response nature of most of these sensors enables the eddy covariance determination of fluxes of heat, momentum, NO_y, CO₂, and O₃ [Wofsy *et al.*, 1993; Goulden *et al.*, 1996; Moore *et al.*, 1996; Munger *et al.*, 1996, 1998].

2.2. Gas Sampling Methods and Protocols

Water soluble gases were sampled with a mist chamber, also known as a nebulizing-reflux chamber [Cofer *et al.*, 1985; Talbot *et al.*, 1990]. A mist chamber concentrates the water soluble gases from a large volume (~1000 L) of air into a small volume (~15 mL) of stripping solution, in this case, ultrapure water was used. The dissolved ions in the stripping solution were quantified by ion chromatography. The mist chamber/ion chromatography (MC/IC) method has been continually developed and improved over the past 10 years and has proven in various intercomparison studies to be very effective at sampling gaseous HNO₃, HCOOH, CH₃COOH, and SO₂ [Keene *et al.*, 1989; Talbot *et al.*, 1990; Stecher *et al.*, 1997].

A Teflon membrane (Zefluor™, Gelman Products Inc.) is used as an aerosol prefilter to prevent water soluble aerosols from being dissolved in the mist chamber stripping solution. A custom-made Teflon filter holder, designed to minimize internal surface area by omitting any backup filter support, attaches directly to the glass inlet of the mist chamber sampler [Klemm and Talbot, 1991]. Operating at a flow rate of 30 standard liters per minute (slpm), this downward-facing prefilter collects a bulk sample of aerosol particles with a diameter between ~10 nm (J. Dibb and B. Anderson, personal communication, 1996) and at least 50 μm for wind speeds up to 5 m s⁻¹ [Davies, 1968; Davies and Subari, 1982]. Aerosol filter samples were stored in a freezer and within a week of

Table 1. Mist Chamber HNO₃ and NH₃ Sampling Dates

Year	Julian Day
1991	165*, 166*, 168, 169*, 223*, 225*, 226*, 227*,
1992	143, 144, 146, 147, 148, 192, 193, 194, 245, 246, 248, 249
1993	62, 79, 80, 81, 118, 119, 121, 200*, 201*, 202*, 203*, 204*
1994	144*, 153*, 154*, 155*, 156*, 161*, 162*, 167*, 168*, 215*, 216*, 217*, 202*, 235*, 236*, 237*, 238*
1995	116*, 117*, 120*, 122*, 159*, 160*, 161*, 164*, 165*, 166*, 167*, 168*, 169*, 213*, 214*, 215*, 219*, 220*, 221*

HNO₃ data collected on all days.

* NH₃ data only collected on these dates.

their collection were treated with 200 μ L of MeOH (to allow more complete wetting of Teflon) and then extracted with two 10 mL aliquots of deionized water. Immediately after their generation, mist chamber samples and aerosol extracts were stored in 30 mL high density polyethylene amber bottles, preserved with 100 μ L of CHCl₃ and kept on ice until their transfer to a refrigerator. All samples were analyzed within 2 months of collection by ion chromatography for major ion species (including NO₃⁻ and NH₄⁺_(aq)). Details of the ion chromatography chemical analysis of water soluble gas and aerosol samples are described by Talbot *et al.* [1992, 1997] and Lefer *et al.* [1994].

The hourly sampling protocol involved collecting 45-50 min integrated mist chamber and aerosol prefilter samples simultaneously from three levels (29, 24, and 11 m above ground) with the remaining 10-15 min available to rinse the mist chambers, to change the prefilters, and to periodically collect mist chamber blanks. Unless otherwise noted, this paper will discuss the gas and aerosol samples collected from the uppermost sampling height at 29 m, some 6-7 m above the canopy. Hourly mist chamber samples were continuously collected for 12-30 hour long periods on 70 dates between 1991 and 1995 (Table 1). The majority of the sampling occurred during the growing season (May - August). The entire Harvard Forest data set, including the University of New Hampshire (UNH) gas and aerosol data, is available on-line via anonymous ftp at io.harvard.edu and the Web site www.as.harvard.edu.

2.3. Potential Sampling Artifacts

Any HNO₃ or NH₃ measurement technique that employs a prefilter is susceptible to certain positive and negative artifacts [Appel and Tokiwa, 1981; Cadle *et al.*, 1982]. The easiest way to minimize prefilter reactions is to sample for a shorter period of time (smaller volume of air), thereby reducing the aerosol loading on the Teflon prefilter. Our 45 min integrated samples (1.3 m³) were relatively short considering that most studies which observed prefilter problems (see below) typically sampled for 6-24 hours integrating much larger volumes of air (5-20 m³).

On a Teflon filter, particulate NH₄NO₃ can volatilize into HNO₃ and NH₃ [Appel *et al.*, 1981] resulting in significant positive HNO₃ [Spicer *et al.*, 1982; Appel *et al.*, 1988] and

NH₃ [Appel *et al.*, 1988] errors. While NH₄NO₃ is volatile at typical tropospheric temperatures and relative humidities [Stelson and Seinfeld, 1982], the reactions producing ammonium (bi)sulfate are generally thought to be irreversible [Tang, 1980]. High levels of acidic sulfate in the eastern United States probably has the effect of reducing atmospheric NH₃ concentrations, by forming involatile ammonium sulfate particles, to values below that required for solid NH₄NO₃ to form. The studies that observed positive HNO₃ and NH₃ artifacts occurred in the western United States where NH₄NO₃ is more prevalent due to lower regional SO₂ emissions [Hidy, 1978; Wolff, 1984]. The substantial SO₄²⁻ wet deposition flux to the northeastern United States [National Atmospheric Deposition Program, 1997] indicates that NH₄NO₃ volatilization should be less of a problem when sampling this generally sulfate rich acidic atmosphere.

A potential negative HNO₃ artifact can occur when HNO₃ reacts with basic soil [Forrest *et al.*, 1982] or sea-salt particles [Savoie and Prospero, 1982] on the prefilter. As suggested above, the northeastern United States aerosol is generally acidic, although this acidity can be mitigated by high soil dust emissions occurring as a result of drought or agricultural practices. Aerosol Ca²⁺ (an indicator of soil dust) and Na⁺ levels on the prefilter were measured for each sample. During this study the mean (\pm standard deviation) mixing ratios of particulate Ca²⁺ and Na⁺ were measured to be 75 \pm 89 ($n=371$) and 287 \pm 370 ($n=425$) pptv, respectively [Lefer, 1997]. While there is no straightforward way to correct gaseous HNO₃ measurements for prefilter reactions with basic particles, 24 HNO₃ samples collected during periods with Na⁺ mixing ratios more than three standard deviations from their mean (i.e., > 1395 pptv) were excluded from the data set. Nine of these 24 high Na⁺ samples were collected on the same day during a rare period of strong easterly winds. It was assumed that the measured loadings of aerosol Ca²⁺ were insufficient to cause a sampling artifact.

Finally, an acidic prefilter will not affect the sampling of acid gases (e.g., HNO₃); however, acidic aerosols could react with NH₃ in the sample airstream. Preliminary lab tests indicate that the relatively low aerosol loading in the 45-50 min sample is not sufficient to be a serious issue. Nevertheless, when trying to measure low levels of NH₃, a prefilter can easily cause problems. No correction to the NH₃ data has been applied for this potential negative artifact.

2.4. Mist Chamber Technical Specifications

This MC/IC gas sampling system had average detection limits of 5 pptv for HNO₃ and 12-40 pptv NH₃, assuming an average solution volume of 15 mL, an average sampled air volume of 1350 L, analytical detection limits (in μ mol/L) of 0.02 (NO₃⁻) and 0.05 (NH₄⁺), and/or a minimum NH₄⁺ concentration of 2 times the average blank of 0.09 μ mol/L. While the mist chambers did not have a detectable NO₃⁻ blank, in some cases there was a slight NH₄⁺ blank associated with the interior mist chamber glass surface that tended to decrease over the course of both single and multiday sampling periods. Since blanks were collected several times a day, this was easily accounted for in the blank correction protocol.

The mist chamber samplers have a shown on multiple occasions to have 100% collection efficiency for HNO₃ [Talbot *et al.*, 1990, 1997]. A single-stage NH₃ dilution system was constructed to determine the mist chamber's collection effi-

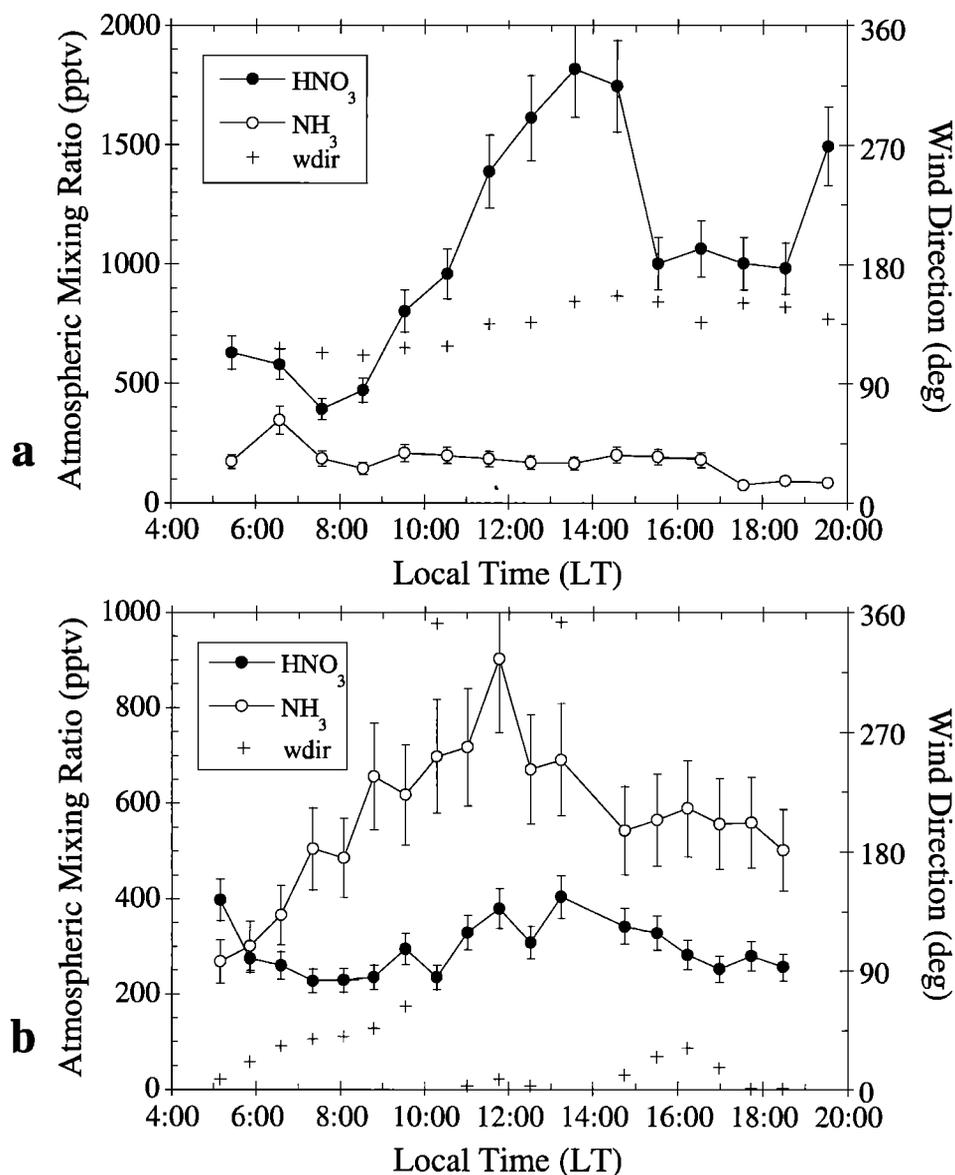


Figure 1. (a) Hourly integrated mixing ratios of HNO₃ and NH₃ and average wind direction for August 3, 1995 (J.D. 215). Error bars represent measurement uncertainty. [b] Same as Figure 1a, but for June 14, 1995 (J.D. 165).

ciency for NH₃. This simple dilution system consisted of (1) a NH₃/N₂ cylinder (~ 1 ppmv) as calibration source, (2) a high-pressure liquid N₂ dewar as a source of diluent gas, (3) two Teledyne-Hastings flowmeters to measure N₂ and NH₃ flows, and (4) a 1.1 m long 2.0 cm ID Pyrex tube sampling manifold with 3.1 mm add port and a 6.35 mm sample port (near opposite ends). The flow rate of the NH₃ cylinder was not measured during an actual calibration run; however, this flow rate was measured before and after each calibration run and always found to be invariant. The concentrated NH₃ was transported via a 1 m length of 1/8" OD Silcosteel™ tubing (Restek Inc.) and added into the core of the N₂ flow. The flow rate and volume of the dilution N₂ was measured by an integrating mass flowmeter upstream from the glass manifold. Approximately 1 m downstream from the NH₃ add port, the NH₃/N₂ mixture was sampled directly from the core of the manifold with a mist chamber.

The NH₃ mixing ratio delivered from the cylinder (821±40 ppbv) was determined by sampling ($n=12$) directly from the Silcosteel™ tubing. The cylinder gas was bubbled through 2 H₂O bubblers in series followed by a mass flowmeter. No NH₄⁺ was ever detected in the second bubbler. For a typical ambient NH₃ mixing ratio (370 pptv), the mist chamber had a mean (\pm standard deviation) collection efficiency of 99% ($\pm 9.2\%$) ($n=9$). Similar NH₃ collection efficiencies were observed for both higher and lower NH₃ levels. A mist chamber collection efficiency of 100% was used for determining the mixing ratios of both HNO₃ and NH₃ in our ambient air measurements.

The uncertainties assigned to the atmospheric mixing ratios reported for MC/IC samples were calculated using the error propagation formula [Knoll, 1979] and applying it to the uncertainties associated with the following measurements: air volume, water volume, ion concentration, blank subtraction,

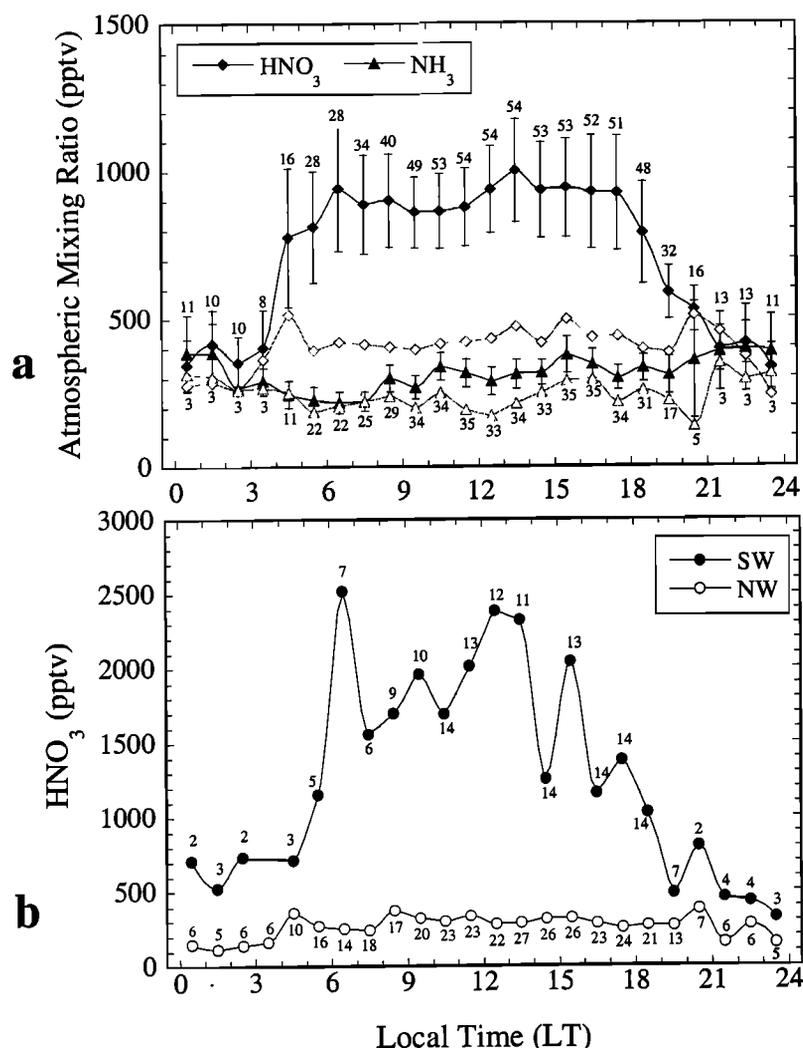


Figure 2. (a) Mean (solid symbols) and median (open symbols) summertime diel cycles of HNO₃ (diamonds) and NH₃ (triangles) for all wind sectors. Error bars represent standard error of mean. Numbers above or below bars are number of hourly samples averaged. (b) Median HNO₃ diel cycles for the dominant wind sectors: 180°-270° is southwest (SW) and 270°-45° is northwest (NW). Values above or below points are number of samples.

and collection efficiency. The reported mixing ratios of HNO₃ and NH₃ have overall uncertainties of $\pm 11\%$ and $\pm 18\%$, respectively. The accuracy of the ion chromatographic determinations of NO₃⁻ and NH₄⁺ in mist chamber samples were referenced to National Institute of Standards and Technology certified aqueous standards; however, at this point there are no certified low-level (sub-ppbv) gaseous standards to directly determine the overall accuracy of any measurement of these and many other trace gases [Crosley, 1994].

3. Results

3.1. Diel Cycles of HNO₃ and NH₃

Changes in mixing ratios of both species were often related to changes in wind direction or the height of the mixed layer, day 215 of 1995 (Figure 1a) is a good example of "typical" diurnal behavior at this site because of consistent winds from the south-southeast throughout the day. Under these conditions, NH₃ levels usually do not vary much while mixing ra-

tios of HNO₃ frequently increase from a morning low to peak at midday, and then decrease throughout the afternoon. Less common at this site is to have north-northeast winds (Figure 1b) which resulted in a distinct NH₃ diel cycle starting with representative NH₃ mixing ratios in the morning, rapidly rising to a midday maximum, which decline throughout the afternoon and evening.

Previous studies have shown that the mixing of polluted and clean air masses commonly results in lognormal distributions of atmospheric species for one specific site, particularly for primary pollutants [e.g., Georgopoulos and Seinfeld, 1982; Parrish et al., 1991]. Both the HNO₃ and NH₃ data sets contained a wide range of lognormally distributed values. Consequently, the mean values may be strongly influenced by a few very high values, in such cases, both mean and median values are plotted. Consolidation and hourly binning of this 1991-1995 summertime data set produced a composite mean diel cycle of HNO₃ at this site that is bimodal with nighttime and daytime mixing ratios of 400 and 900 pptv, respectively

(Figure 2a). The composite median HNO₃ diel cycle displays less variability (Figure 2a) on account of the low HNO₃ mixing ratios in NW surface winds (Figure 2b), which occurred twice as often as SW winds during our sampling (see Figure 2b and section 4.1). The same data processing procedure yielded composite average and median NH₃ diel cycles that show mixing ratios consistently in the 200-400 pptv range (Figure 2a).

3.2. Wind Sector and Season

Diel changes in the HNO₃ mixing ratio for the southwest (SW) and northwest (NW) wind sectors are of the order of 2000 and 500 pptv, respectively (Figure 2b). In addition to having a lower amplitude, the NW diel cycle also starts from lower baseline HNO₃ mixing ratios. This pattern matches that previously noted by *Munger et al.* [1996], for NO_y and NO_x, who defined the primary surface-wind direction sectors at this

site as the north-northwesterly (270°-45°), the southwesterly (180°-270°), and the easterly (45°-180°). The NH₃ diel cycle did not change as a function of wind sector (not shown). However, mean and median mixing ratios of NH₃ and HNO₃ are different for the NW and SW wind sectors (Table 2). On average, an air mass with surface winds from the SW wind sector contains 3-4 times more HNO₃ and significantly less NH₃ ($p = 0.038$) than one with winds from the NW wind sector (Table 2).

Since a backwards trajectory analysis was not performed for these sample periods, it is difficult to ascribe a specific source region to a particular gas sample. However, it is possible to observe that easterly winds from the general Boston metropolitan area were quite rare during our sampling and were commonly associated with low-pressure systems off the coast. A situation where "fresh" industrial emissions could have been rapidly transported to the site during overcast conditions consequently resulting in low HNO₃ (Figure 3) and high NO_x mixing ratios [*Munger et al.*, 1996].

Over a 5 year period the majority (66%) of HNO₃ samples were collected in the summer (June, July, August) while 23% and 10% of the samples were collected in spring (March, April, May) and fall (September, October, November), respectively. No samples were collected in the winter (December, January, February). The measured HNO₃ mixing ratios were lowest in early spring (Figure 4a) and highest in late summer to early fall (days 210-240 of 1994). The NH₃ levels peak in July and August (Figure 4b) with lower mixing ratios observed in the spring. An exponential relationship ($r^2 = 0.82$) between NH₃ levels and air temperature is evident for the summer of 1995 (Figure 5). At times the temperature dependence of the NH₃ breaks down, as shown for August 1995 (Figure 5). Data from other earlier years contain similar dual temperature relationships, but for purposes of clarity, only one year of summertime NH₃ data is included in Figure 5.

Table 2. Summary Statistics of Mixing Ratios at UNH Sampling Times and Selected Surface Wind Direction Sectors

Statistic	All Samples	NW	E	SW
<i>HNO₃, pptv</i>				
<i>n</i>	766	367	146	177
25%	211	154	279	453
Median	410	273	476	1239
Mean	817	484	650	1700
s.d.	1025	587	532	1533
75%	984	539	854	2534
<i>NH₃, pptv</i>				
<i>n</i>	463	234	90	113
25%	142	179	133	124
Median	245	281	194	224
Mean	231	353	309	292
s.d.	254	260	229	266
75%	452	471	467	436
<i>NO_x, pptv</i>				
<i>n</i>	443	231	110	81
25%	782	641	1406	1979
Median	1458	910	3396	4078
Mean	3647	1340	5214	8080
s.d.	7011	1221	6737	12844
75%	3794	1522	6091	7497
<i>NO_y, pptv</i>				
<i>n</i>	662	359	135	156
25%	1861	1485	3228	3616
Median	3481	2290	4484	5592
Mean	5191	3038	6871	8655
s.d.	5947	2428	5875	9022
75%	6099	3772	8557	10972
<i>{NO_y-NO_x}, pptv</i>				
<i>n</i>	395	227	92	69
25%	992	976	933	1015
Median	1793	1629	2095	2457
Mean	2466	1985	2952	3429
s.d.	2266	1468	2963	2942
75%	3017	2548	3412	5483

Northwest (NW) is 270°-45°, East (E) is 45° - 180°, and Southwest (SW) is 180°-270°. Statistics include number of samples (*n*), 25th percentile (25%), standard deviation (s.d.), and 75th percentile (75%).

4. Discussion

4.1. Representativeness of the Composite Data Set

To extract meaning from a noncontinuous data set it is necessary to determine what time period the composite data set most closely represents. Certainly, the mean and median values reported in Table 2 are not necessarily comparable to overall annual values due to the lack of wintertime (December - February) data (Table 1). Due to the availability of a continuous data set of many chemical species and meteorological parameters made by Harvard University (HU) from the same tower, [e.g., *Munger et al.*, 1996, 1998] we can investigate how a parameter measured more or less continuously between 1991 and 1995 compares to the same parameter analyzed only for the UNH composite sampling times.

Measurements of wind direction reveal that NW winds occur 49% and 52% of the time for continuous (HU) and composite (UNH) sampling, respectively. Similar good agreement is observed for the E and SW windsectors (Table 3). However, it appears that the SW sector is underrepresented ($\Delta -12\%$) and NW similarly over represented ($\Delta 8\%$) in the composite data set when compared to summer-only HU observations (Table 3). On a diel basis, the median NO_y measured during UNH sampling times compares well with the median summertime NO_y diel (Figure 6), with the greatest differences occurring in the nighttime hours when UNH sample coverage

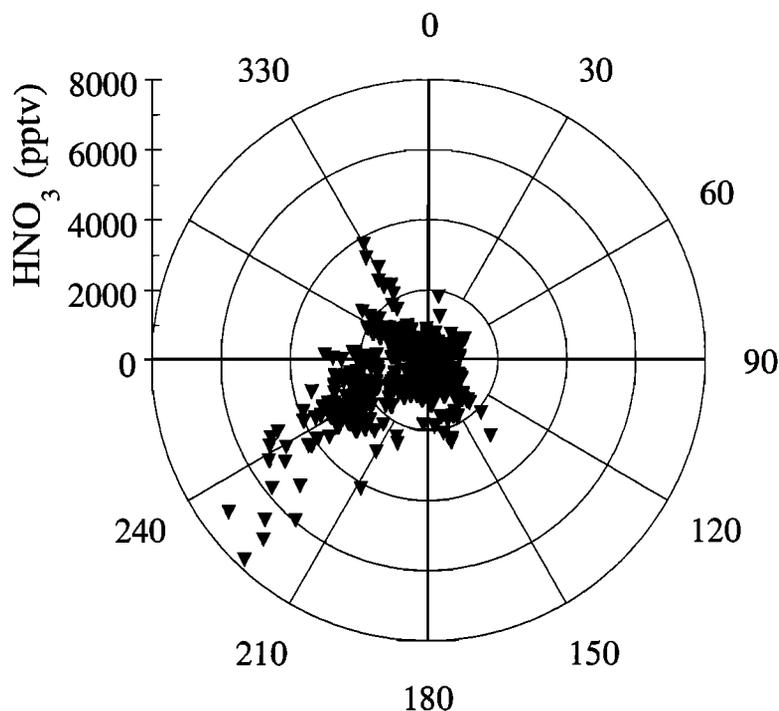


Figure 3. HNO₃ mixing ratios ($n = 711$) as a function of average hourly wind direction (degrees). HNO₃ mixing ratio uncertainty of $\pm 11\%$ not shown to improve readability.

was the lightest (Figure 2a). Summer and winter NO_y diel cycles vary considerably [Munger *et al.*, 1996]; consequently, the UNH composite NO_y diel cycle between 0900 and 1300 is significantly different ($p < 0.05$) from the 1991-1995 mean annual NO_y diel. Overall, the composite data set is most representative of summer conditions between the hours of 0500 and 2000 with a bias toward air masses with surface winds from the cleaner NW sector.

4.2. HNO₃

4.2.1. Comparison to other measurements. Table 4 is a compilation of HNO₃ measurements in rural North America, sorted in order of increasing sample integration time. This list, while not exhaustive, represents some of the more recent measurements. All the results, with the exception of this study, were obtained using Teflon/Nylasorb filterpacks which have previously been shown to compare reasonably well to the MC/IC technique [Talbot *et al.*, 1990]. When comparing these values, note that all the subdaily measurement campaigns mainly occurred during the summer months. Many of these high-resolution projects do not include nighttime measurements (as noted in Table 4) which are generally lower [Edgerton *et al.*, 1992] and may be biased by nonrepresentative meteorological conditions. While the daily and weekly HNO₃ sampling programs provide excellent seasonal and annual coverage, the long integration times may mask hourly and day/night variability that is useful in understanding the processes influencing the atmospheric chemistry of HNO₃.

The overall hourly mean and median HNO₃ mixing ratio for Harvard Forest agrees quite well with other measurements in rural North America (Table 4). The large range of HNO₃ mixing ratios (26-7771 pptv) at Harvard Forest is indicative

of the wide variety of air masses that influence this site. The smaller HNO₃ variability reported in most other studies is to some degree a consequence of longer sample integration times, especially the weekly sampling of the National Dry Deposition Network [Edgerton *et al.*, 1992] which has now been incorporated into the EPA Clean Air Status and Trends Network (CASTNet). Ollinger *et al.* [1993] noted that mean HNO₃ levels for the CASTNet sites in the northeastern United States decreased linearly with increasing latitude. Interestingly, Harvard Forest at 42.5°N with a mean hourly mixing ratio of 828 pptv fits this trend (Table 4). The gradient of decreasing HNO₃ values to the north of this site concurs with the calculations of Munger *et al.* [1998], who concluded that much of the NO_x emitted in the northeastern United States is deposited as HNO₃ within a few days.

4.2.2. HNO₃ diel trends. HNO₃ mixing ratios are lower at night and higher during the day at Harvard Forest (Figure 2a) and at other sites as well [Edgerton *et al.*, 1992; Parrish *et al.*, 1986]. Previous attempts to define the diel cycle of HNO₃ have shown similar patterns, with the highest mixing levels occurring in the afternoon [Parrish *et al.*, 1986; Aneja *et al.*, 1994a, Kleinman *et al.*, 1994]. The distinctly different HNO₃ diel patterns for the SW and NW windsectors emphasize the respective urban and rural source regions for these air mass categories (Figure 2b). Earlier studies at Harvard Forest [e.g. Munger *et al.*, 1996] labeled the SW and NW surface wind direction sectors as “polluted” and “clean” based on significantly higher midday NO_x and NO_y mixing ratios for the SW sector. Using a trajectory model, Moody *et al.* [1998] quantitatively determined the same air masses source regions and described their divergent chemical climatologies. Instead of using a meteorological parameter, Kleinman *et al.* [1994]

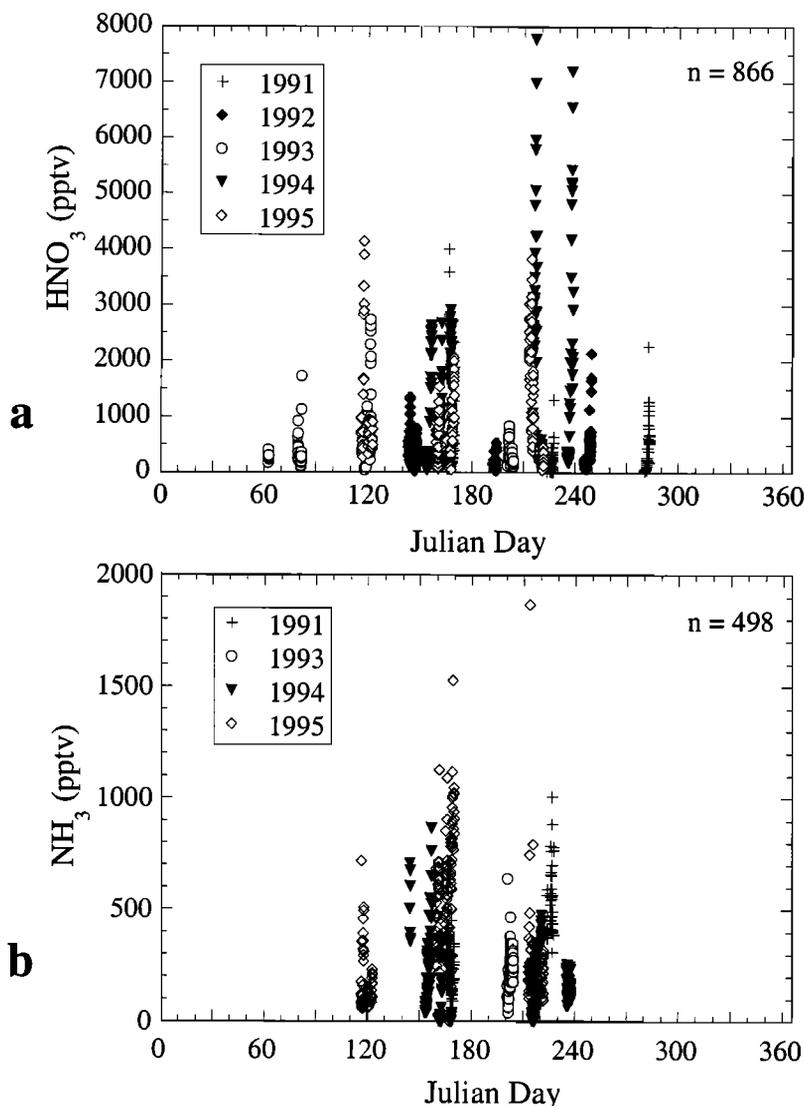


Figure 4. (a) Hourly integrated HNO₃ mixing ratios plotted versus Julian day. All samples collected between 1991 and 1995 on days listed in Table 1. Measurement uncertainty of $\pm 11\%$ not shown to keep figure legible. (b) Same as Figure 4a, except for NH₃. Measurement uncertainty of 17% not shown.

subdivided HNO₃ data from rural Georgia into groups based on O₃ mixing ratios and in the process produced two HNO₃ diel patterns of similar shape and magnitude to those in Figure 2b.

The notable rise in early morning HNO₃ mixing ratios (~ 0500 LT) (Figures 2a and 2b) is coincident with average time of summer sunrise as well as large increases in the heat flux, friction velocity, NO_x and NO_y mixing ratios, and NO_y deposition rate [Munger *et al.*, 1996]. Due to low photochemical activity at this time of day, it is likely that this increase in HNO₃ could result from the entrainment of HNO₃ in "fossil" mixed layer air from the previous day as the new mixed layer develops [Kleinman *et al.*, 1994]. Large increases in early morning NO_y deposition velocities [Munger *et al.*, 1996] endorse this theory by demonstrating high concentrations of a readily depositing NO_y species (e.g., HNO₃) in these air masses. Trainer *et al.* [1991] predict that some of the HNO₃ mixed down as the nocturnal boundary layer erodes is produced at night via heterogeneous reactions involving N₂O₅.

4.2.3. Seasonal differences in HNO₃. Munger *et al.* [1998] analyzed 7 years (1990-1996) of continuous hourly NO_y flux measurements at this site and report the highest NO_y deposition occurs during the months of May, July, and August and the lowest during December, January, and February. As the primary depositing species of NO_y, the composite HNO₃ seasonal cycle (Figure 4a), while lacking wintertime data, is consistent with these findings. Parrish *et al.* [1986] also report their maximum and minimum HNO₃ levels in late summer and winter, respectively. However, other studies from other regions have observed the significantly different HNO₃ seasonal cycles. In Cedar Creek, Wyoming, the highest levels occur in the spring [Edgerton *et al.*, 1992], while Bondville and Argonne, Illinois experience their peak HNO₃ concentrations in the winter [Meyers *et al.*, 1991]. Seasonal differences in HNO₃ are believed to be a function of many interrelated physical and climatological factors which may also differ seasonally and geographically, including: homogeneous and heterogeneous production, dry deposition and wet removal, local

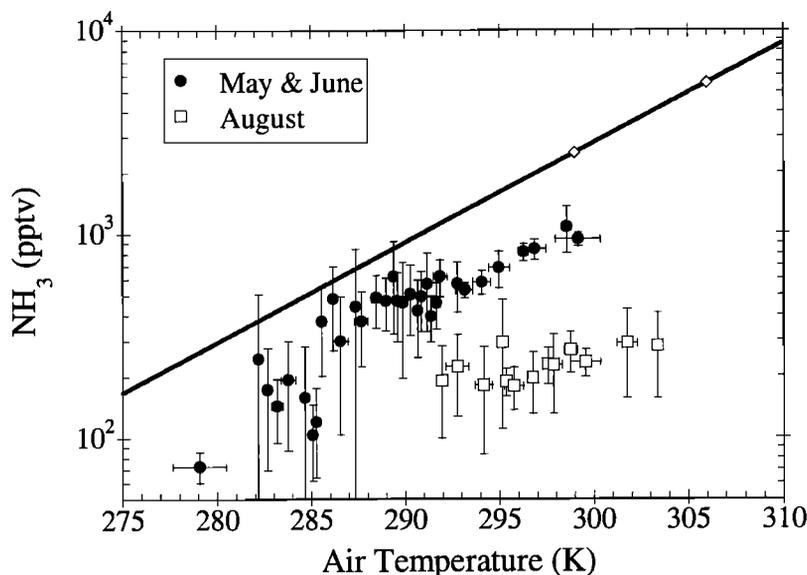


Figure 5. Temperature dependence of gaseous NH₃ mixing ratios collected for two different periods in the summer of 1995: May 1 to June 18, 1995 (May, June) and August 1-9, 1995 (August). Each symbol represents the average of five individual 1 hour measurements spanning the temperature range indicated by the horizontal bars. The vertical bars represent the standard deviation of the five samples. The solid line corresponds to the calculated NH₃ vapor pressure above a solution with 46 μM [NH₄⁺] and pH 6.8 [Farquhar *et al.*, 1980].

biogenic isoprene emissions, boundary layer dynamics, and regional NO_x emission densities.

While the weekly CASTNet samples will probably not be useful to determine the importance of some of these factors such as nighttime heterogeneous HNO₃ production, it is a good data set to examine seasonal HNO₃ levels across the eastern United States. The 1994 data from two northeastern United States CASTNet sites (Howland, Maine and Abington, New York) were selected to highlight the two extremes in the regional HNO₃ latitudinal gradient. In 1994, both of these sites report the highest sustained HNO₃ levels in July and August (~ days 180-240) (Figure 7) and lower mixing ratios in the winter, which is consistent with the HNO₃ and NO_y deposition results at Harvard Forest [this study; Munger *et al.*, 1998]. Peak July and August HNO₃ mixing ratios at Harvard Forest and other northeastern sites may be explained by additional HNO₃ production via organic nitrate pathways [Munger *et al.*, 1998]. The coherence of the HNO₃ signals from these two sites, for both the long- and short-term (episodic) events,

Table 3. Frequency of Average Hourly Surface Winds by Sector (1991-1995)

	n	Frequency, %		
		NW	E	SW
UNH ^a	720	52	20	27
1991-1995 ^b	33330	49	19	32
Summer (1991-1995) ^c	8466	44	16	39

Northwest (NW) is 270°-45°, East (E) is 45°-180°, and Southwest (SW) is 180°-270°.

^aUniversity of New Hampshire (UNH) HNO₃ and NH₃ sampling times.

^bHarvard University continuous measurements.

^cSummer is defined as June, July, and August.

suggests that similar factors control the HNO₃ levels throughout the northeastern United States. The regional HNO₃ concentration gradient reported by Ollinger *et al.* [1993] is also evident in these two records and most likely represents the deposition of HNO₃ as a large portion of the emitted NO_x is oxidized to HNO₃ and deposited within the region [Munger *et al.*, 1998].

4.3. NH₃

4.3.1. Comparison to previous NH₃ measurements. The mean NH₃ mixing ratio of 321 pptv is equivalent to the 300 and 420 pptv summertime mean observed for other forested sites in Oak Ridge, Tennessee and Niwot Ridge, Colorado [Langford *et al.*, 1992]. At Harvard Forest, 10 years previous to this study, Tjepkema *et al.* [1981] observed summertime NH₃ mixing ratios in the range of 200-330 pptv using 7 day oxalic acid denuder measurements. The greater variability displayed in our hourly measurements is due to the damping of high-frequency structure by the weekly integrated samples.

Our composite NH₃ diel cycle does not display the trend of higher daytime mixing ratios peaking in the afternoon and then gradually declining throughout the night observed at several other sites [Langford *et al.*, 1992]. Some of the individual days that went into this composite do, however, demonstrate such a pattern, including day 165 of 1995 as shown in Figure 1b. Interestingly, some days with a flat NH₃ diel cycle display a more "typical" NH_x (NH₃ + NH₄⁺) diel signal (Figure 8a).

Our composite of summer NH₃ levels generally fits in with the complete year of NH₃ concentrations measured by Tjepkema *et al.* [1981] at Harvard Forest in 1980. They found the highest NH₃ levels to occur in the summer, peaking in early August and decreasing rapidly to fall and winter lows of less than 50 pptv. As suggested by the "typical" seasonal and diel cycles of NH₃, boundary layer NH₃ levels are a general func-

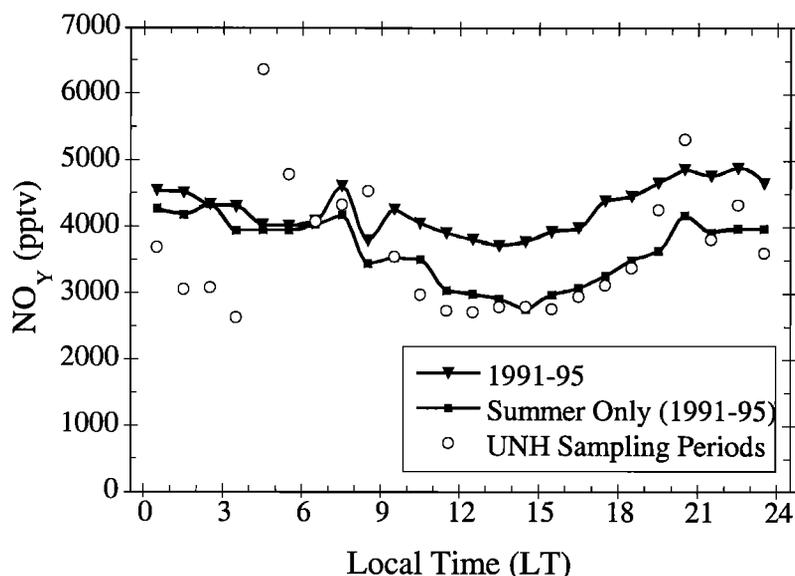


Figure 6. Median diel cycles of NO_y between 1991 and 1995 for three different sets of data: all data; summertime only (June, July, and August); and UNH HNO₃ sampling periods listed in Table 1. Number of samples in each hourly group is \approx 1200 for 1991 and 1995 and \approx 350 for summer only. UNH sample number shown in Figure 2a for HNO₃ sampling times.

tion of air temperature, with higher NH₃ mixing ratios associated with warmer temperatures [Langford *et al.*, 1992]. Our observations of small, or no, diel variation of NH₃ mixing ratios on many days suggests that other factors also play a significant role in regulating NH₃ levels at the Harvard Forest.

4.3.2. Controls on boundary layer NH₃ levels. It is clear that air temperature is a primary controller of NH₃ in the boundary layer, as several other sites show a strong temperature dependence on NH₃ mixing ratios [Langford *et al.*, 1992]. Higher air temperatures lead to greater emissions of NH₃ from its primary sources, cattle feedlots and fertilizer applications. As ambient NH₃ mixing ratios above vegetated

systems approach the NH₃ compensation point, higher air temperatures increase the vapor pressure of NH₃ above the NH₄⁺ dissolved in the water film lining stomatal cavities, increasing the NH₃ emitted by the canopy as predicted by Henry's Law [Langford and Fehsenfeld, 1992]. At Harvard Forest, due to the lack of nearby sources and high levels of SO₄²⁻ in the atmosphere, the ambient mixing ratios of NH₃ are more or less always below the NH₃ compensation point reported by Farquhar *et al.* [1980], suggesting that the canopy (or ecosystem) at Harvard Forest may be continually losing NH₃ to the atmosphere. Similarly, based on the low nature of the few NH₃ mixing ratios reported for eastern forests, Lang-

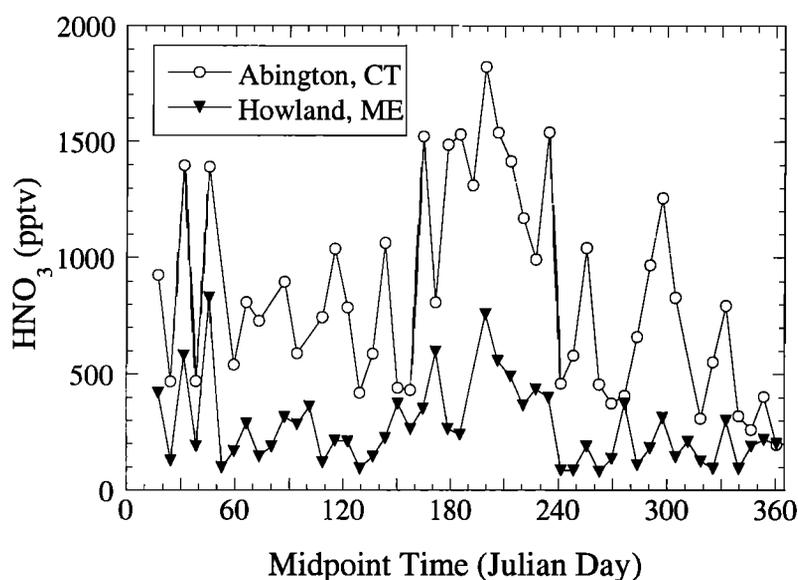


Figure 7. Weekly integrated HNO₃ mixing ratios for 1994 for two northeastern sites. Data are from U.S. EPA Clean Air Status and Trends Network (CASTNet) sites in Abington, Connecticut (ABT147) and Howland, Maine (HOW132) [Clean Air Status and Trends Network, 1997].

Table 4. Nitric Acid Mixing Ratios for Various Sites in Rural North America

Site (Latitude)	Mean \pm s.d. (Median \pm MAD)	Range	Integration (Restrictions) Study Period	Method	Source
Harvard Forest, Massachusetts (42.5°N)	828 \pm 1045, (423 \pm 257)	26-7771	1 hour (episodic), Summers 1991-1995	Mist Chamber	This Study
Candor, North Carolina (35.3°N)	670 \pm 330	30-1760	1 hour (daytime only), June-July 1992	Teflon/nylon filter pack	Aneja et al. [1994b]
Metter, Georgia (32.4°N)	800		1 hour, June - August 1991	NO _y -NO _x with nylon Filter (includes particulate NO ₃)	Kleinman et al. [1994]
Mt. Mitchell, North Carolina (35.8°N)	406 \pm 340 (1988) 498 \pm 210 (1989)	20-2000	2 hours (daytime only), summers 1988-1989	Teflon/nylon filter pack	Aneja et al. [1994a]
Niwot Ridge, Colorado (40.3°N)	----	10-3000	1-4 hours (daytime only), all seasons 1979-84	Teflon/nylon filter pack	Parrish et al. [1986]
Oak Ridge, Tennessee (36.0°N)	1649	697-2819	4 hour (daytime only), September 1982	Teflon/nylon filter pack	Meyers et al. [1989]
Calgary, Alberta (51.0°N)	420	20-4000	4 hours (daytime only), June-August 1982	Teflon/nylon filter pack	Peake et al. [1985]
Pittsburg, California (38.0°N)	----	300-1500	8 hours, February 1979	Teflon/nylon & Teflon/NaCl filter pack	Appel et al. [1980]
Whiteface Mountain, New York (44.3°N)	200 (clean) 1000 (polluted)	100-3100	6/12 hours, July 1982	Teflon/NaCl filter pack & diffusion denuder	Kelly et al. [1984]
State College, Pennsylvania (40.8°N)	900 (January) 400 (February) 500 (March)	50-1400 (January) 100-810 (February) 100-2295 (March)	24 hours (15 days/month), January-March 1984	Teflon/nylon filter pack downstream of NH ₃ denuder	Lewin et al. [1986]
Niwot Ridge, Colorado (40.3°N)	64 (Winter) 238 (Summer)	20-700	24 hours (episodic), All Seasons 1980-1984	Teflon/nylon filter pack	Parrish et al. [1986]
Howland, Maine (45.2°N)	270 \pm 174 ^a 425 \pm 154 ^b	79-829 ^a 154-329 ^b	7 days, January 1993- present	Teflon/nylon filter pack	CASTNet
Woodstock, New Hampshire (43.5°N)	241 \pm 123 ^a 256 \pm 80 ^b	58-605 ^a 162-398 ^b	7 days, January 1989- present	Teflon/nylon filter pack	CASTNet
Lye Brook, Vermont (43.0°N)	677 \pm 331 ^a 733 \pm 218 ^b	201-1409 ^a 352-1124 ^b	7 days, April 1994-present	Teflon/nylon filter pack	CASTNet
Connecticut Hill, New York (42.4°N)	921 \pm 324 ^a 1038 \pm 359 ^b	297-1911 ^a 612-1911 ^b	7 days, October 1987- present	Teflon/nylon filter pack	CASTNet
Catskills, New York (42.4°N)	975 \pm 412 ^a 1165 \pm 232 ^b	291-1665 ^a 736-1615 ^b	7 days, May 1994-present	Teflon/nylon filter pack	CASTNet
Abington, Connecticut (41.9°N)	842 \pm 430 ^a 1232 \pm 440 ^b	197-1822 ^a 430-1822 ^b	7 days, December 1994- present	Teflon/nylon filter pack	CASTNet

All mixing ratios reported as pptv.

CASTNet is the Clean Air Status and Trends Network [1997]. Only selected New England sites of CASTNet are presented.

^a Annual for 1994.^b Summer for 1994.

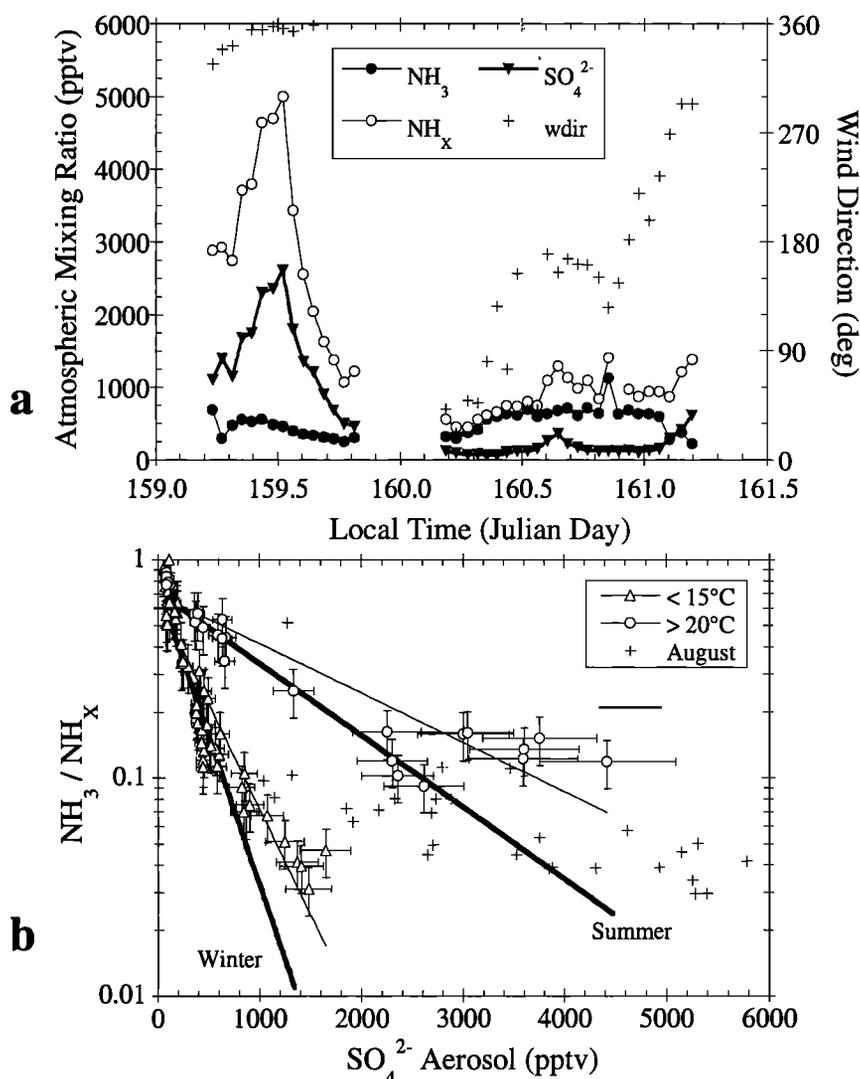


Figure 8. (a) Dependence of gaseous/particulate partitioning of ammonia on atmospheric sulfate. Wind direction and hourly NH₃ and NH_x and aerosol SO₄²⁻ mixing ratios for June 8 and 9, 1995 (J.D. 159 and 160). Measurement uncertainty not shown. (b) Dependence of NH₃/NH_x partitioning on atmospheric sulfate and air temperature. Open symbols represent samples collected in May and June 1995 at two different temperature ranges ($\leq 15^{\circ}\text{C}$ (triangles) and $\geq 20^{\circ}\text{C}$ (circles)). Vertical bars show the uncertainty of the partition ratio as determined by propagation of errors. Horizontal bars represent SO₄²⁻ measurement uncertainty. Pluses correspond to August 1995 samples. Error bars for these samples are not shown to keep figure legible. Thick lines represent relationships reported by Langford et al. [1992] from a compilation of winter and summer results.

ford et al. [1992] predicted these ecosystems could emit significant levels of NH₃.

For the months of May and June of 1995, the exponential relationship between averaged NH₃ mixing ratios and temperature ($r^2=0.85$) may perhaps define the NH₃ compensation point for this ecosystem. If so, this particular NH₃ compensation point is lower than that previously observed by Farquhar et al. [1980] for snap beans and confirmed by Langford and Fehsenfeld [1992] for a lodgepole-ponderosa pine/ spruce-fir forest. The Farquhar et al. [1980] NH₃ compensation point is plotted as a function of air temperature for comparison (Figure 5).

Another fundamental determinant of NH₃ levels at most sites is their proximity to NH₃ sources. With mean and median mixing ratios between 200 and 350 for all wind sectors,

this suggests that there are few significant sources of NH₃ near Harvard Forest. While mean NH₃ levels from the "clean" NW sector are significantly greater than those from the "polluted" SW sector, total NH_x levels, and therefore total NH₃ emissions, are greater in the SW wind sector. Thus significant levels of NH₃ are emitted from the SW sector; however, a large fraction of the NH₃ is soon converted to NH₄⁺_[p], resulting in low ambient NH₃ mixing ratios.

As described earlier in section 2.3, NH₃ can rapidly react with H₂SO₄ to produce ammonium (bi)sulfate aerosols. In an acidic atmospheric environment dominated by SO₄²⁻, Tang [1980] predicted that a primary control on the gaseous/particulate partitioning of ammonia is the level of atmospheric SO₄²⁻. This control is clearly demonstrated by comparing two consecutive days (J.D. 159-160) in 1995. On day

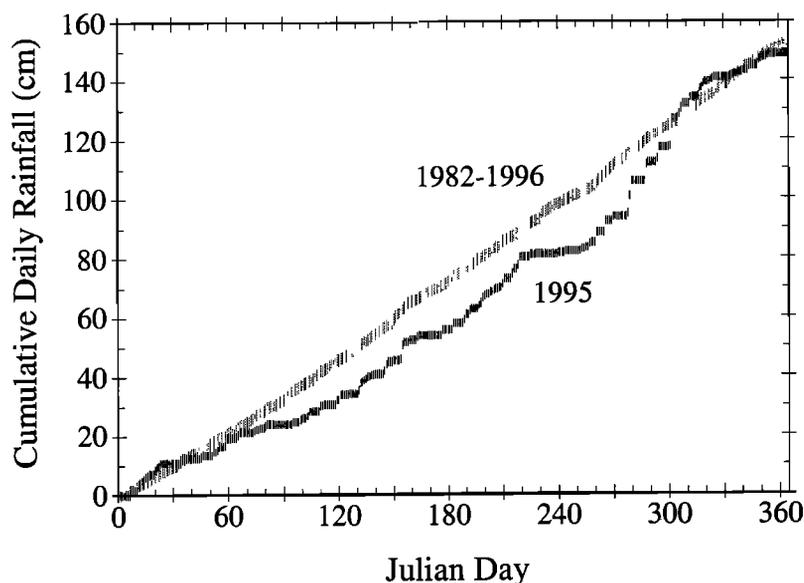


Figure 9. Cumulative daily rainfall at the Quabbin Reservoir National Atmospheric Deposition Program site for 1995 and 14 year average for years 1982-1996 [National Atmospheric Deposition Program, 1997].

159 (1995), north winds brought high levels of NH_x (3-5 ppbv) and high SO₄²⁻ levels (~1-2 ppbv) to Harvard Forest (Figure 8a) and NH₃ accounts for 9-25% of NH_x. On day 160, easterly winds advected moderate levels of NH_x (~500-800 pptv) and very little aerosol SO₄²⁻ (<500 pptv) resulting in the opposite situation with the majority of the NH_x (67-91%) present as NH₃ instead of aerosol NH₄⁺ (Figure 8a).

Average aerosol SO₄²⁻ mixing ratios for the "polluted" SW sector are 2.3 times higher than the NW sector, resulting in significantly different ($p < 0.001$) mean (\pm standard deviation) NH₃/NH_x ratios of 0.39 (± 0.22) and 0.23 (± 0.22) for the NW and SW wind sectors, respectively. Langford *et al.* [1992] collected available data from various studies which simultaneously determined NH₃, NH₄⁺, and SO₄²⁻ mixing ratios. Breaking up the data into wintertime and summertime measurements, they observed negative exponential relationships between the fraction of NH_x as NH₃ and total atmospheric sulfate. The steeper slope of the wintertime data was attributed to decreased wintertime NH₃ emissions and the lower equilibrium vapor pressure of NH₃ over ammonium sulfate aerosols at colder temperatures.

Separating our May and June 1995 NH₃ data into two groups based on the air temperature, $\leq 15^\circ\text{C}$ and $\geq 20^\circ\text{C}$, we observed exponential relationships describing the partitioning of NH₃ and NH₄⁺ as a function of SO₄²⁻_[p] (Figure 8b). The squared correlation coefficients are 0.85 and 0.90 for the $\leq 15^\circ\text{C}$ and $\geq 20^\circ\text{C}$ groups, respectively. These relationships are quite similar to those reported by Langford *et al.* [1992], which, for comparison, have been included in Figure 8b (thicker lines). Not included in this analysis, but also shown in Figure 8b, are NH₃ data from August 1995. All the data collected during August represent sampling periods in which the air temperature was 19°C or greater. With the exception of the samples with quite high SO₄²⁻ mixing ratios (> 3500 pptv), most of the remaining August samples fall somewhere between the $\leq 15^\circ\text{C}$ and $\geq 20^\circ\text{C}$ ammonia-to-sulfate relationships described above. August 1995 is the same period for

which the relationship between NH₃ and temperature shown in Figure 5 does not apply.

In addition to being a warmer time period (Figure 5), the August samples also contained on average significantly more SO₄²⁻ and less NH₃ relative to NH₄⁺ (Figure 8b). However, the majority of the August samples were collected within temperature and SO₄²⁻ ranges observed during summer and still contained less NH₃ (Figures 5 and 8b). Langford and Fehsenfeld [1992] also observed a deviation from the predicted compensation point at higher temperatures and speculated that lower NH₃ emissions were related to water stress. At Harvard Forest, 1995 was drier than average with a period of drought occurring from early August through mid-September as shown by cumulative daily rainfall (Figure 9). These data further suggest that for vegetation experiencing water (or other physiological) stress, which encourages reduced stomatal apertures, the exchange of NH₃ is also restricted, effectively suppressing a plant's NH₃ compensation point.

Alternatively, recent studies have investigated the equilibrium vapor pressure of NH₃, HNO₃, or H₂SO₄ over ammonium nitrate and ammonium sulfate solutions [e.g., Clegg *et al.*, 1998]. For our data set, the product (K) of [HNO₃] and [NH₃] is considerably lower than the calculated ammonium nitrate dissociation constant (K_c) of Stelson and Seinfeld [1982] at all relative humidities and temperatures. Studies by Marti *et al.* [1997] have shown that the vapor pressure of H₂SO₄ decreases dramatically when NH₃ is added to the sulfuric acid solution, suggesting that the vapor pressure of NH₃ over ammonium (bi)sulfate could also be low. A proper analysis of this complex multiphase system is beyond the scope of this paper and will hopefully be thoroughly investigated in a future study.

4.4. NO_y and HNO₃

The NO_y diel cycle at Harvard Forest, with lower mixing ratios at midday and higher levels at night, has been attributed

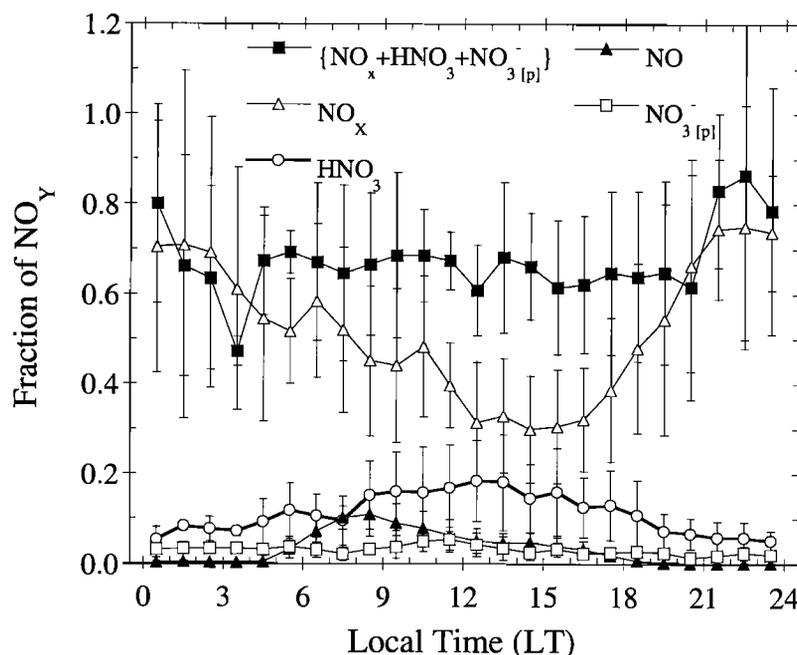


Figure 10. Median partitioning ratio of individual and sum of measured NO_y species as a function of time of day. Vertical bars represent median absolute deviation (MAD). Sample numbers for this composite diel are the same as HNO₃ diel in Figure 2a.

to changes in the height of the boundary layer and the vertical distribution of NO_y [Munger *et al.*, 1996]. At night, local anthropogenic NO_x emissions accumulate below the stable nocturnal boundary layer. As the mixed layer grows the next morning, boundary layer NO_y concentrations are diluted by the entrainment of air lower in NO_y from aloft. For the UNH sampling periods this process resulted in median midday and midnight NO_y mixing ratios of ~ 3000 and 4000 pptv, respectively (Figure 6). The range of NO_y values and diel trend are similar to those observed at other flatland rural sites in North America [Parrish *et al.*, 1993].

Four of the individual component species of NO_y (NO, NO₂, HNO₃, and NO₃⁻_[p]) were simultaneously measured at Harvard Forest. NO and NO₂ rapidly interconvert between each other as function of actinic flux, oxidant concentrations (O₃ and peroxy radicals), and temperature [Parrish *et al.*, 1993]. Thus when considering a composite data set collected under a variety of conditions, it is more meaningful to look at NO_x, the sum of NO and NO₂. NO_x is, at all times, the largest fraction of NO_y at Harvard Forest (Figure 10).

At night NO_x accounts for more than 60% of NO_y while no other measured species contributes more than a 10% share of NO_y (Figure 10). Nitric acid is the next most abundant measured NO_y species with a midday maxima of 20% of NO_y occurring at the same time as the NO_x minima, indicative of the photochemical oxidation of NO₂ to HNO₃. At night, all the NO in the surface layer is titrated to NO₂ by reaction with O₃ and other oxidants. As the Sun rises, NO₂ photolysis begins and the NO contribution increases from essentially zero to a high of about 10% of NO_y around 0800 LT (Figure 10). Aerosol NO₃⁻ is a minor fraction of NO_y at this site accounting for 3-7% of NO_y at any time of the day.

The sum of these four NO_y species (ΣNO_{y(i)}) accounted for 60-80% of NO_y, with the median of the unmeasured residual

remaining fairly constant (~ 1500-2500 pptv) throughout the day (Figure 10). In air masses with winds from the urban SW wind sector, the mean (± standard deviation) “unmeasured” NO_y fraction (NO_y - ΣNO_{y(i)}) was 23% (±14%) of NO_y. The “unmeasured” NO_y fraction accounted for approximately 40% ± 20% of the NO_y in surface winds from the rural areas to the NW and from the Boston metropolitan area to the east. Typically, NO_x, HNO₃, and PAN are the major reactive nitrogen species at most sites [Parrish *et al.*, 1993]. Recent studies suggest that various other organic nitrates may also be an important component of NO_y at forested sites [Trainer *et al.*, 1991]. The majority of the “unmeasured” NO_y at Harvard Forest is most likely PAN and other organic nitrates. In contrast to HNO₃, PAN is only a temporary NO_y reservoir since it thermally decomposes back to NO_x. For a site in Scotia, Pennsylvania, situated in an oak forest, midday summertime PAN mixing ratios can get as high as 2000 pptv and can account for as much as 30-40% of NO_y [Trainer *et al.*, 1991]. Oak forests like Harvard Forest emit large amounts of isoprene in the summer months [Goldstein *et al.*, 1998]. Since the oxidation products of isoprene are thought to be important precursors of PAN [Trainer *et al.*, 1991], one would expect significant PAN levels at Harvard Forest. Since it quickly degrades at summertime surface temperatures, PAN tends to have a diel cycle similar to HNO₃. The diel cycle of the NO_y residual does appear to decrease in the evening (2200-0100) as expected (Figure 10). However, the larger variability in the nighttime values due to the lower sampling coverage make this a non-significant difference.

The quantity {NO_y-NO_x} describes the sum of HNO₃, PAN, and other oxidized reactive N species. The linear relationship between HNO₃ and {NO_y-NO_x} (slope = 0.55, r² = 0.86) indicates that HNO₃ is typically about half of the oxidized NO_y in air masses arriving from the SW wind sector

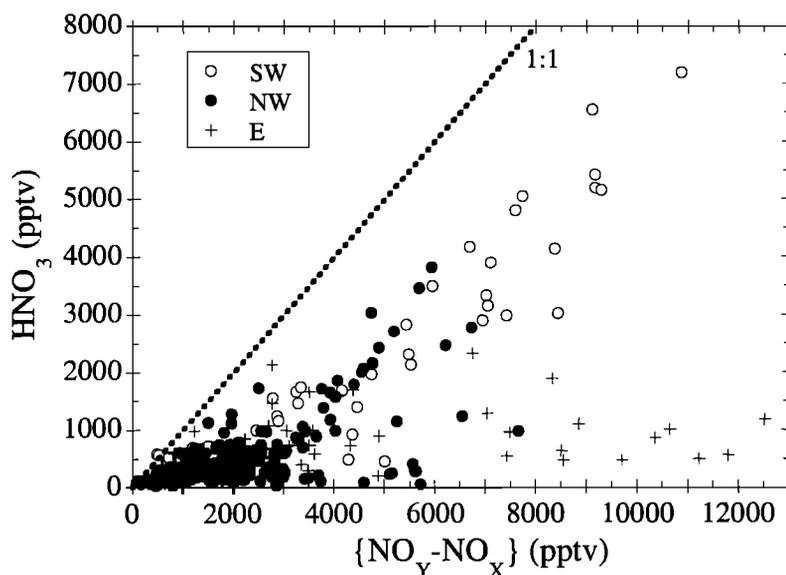


Figure 11. Relationship between HNO₃ and oxidized fraction of NO_y, defined as {NO_y-NO_x}, for the three surface wind sectors: 180°-270° is southwest (SW); 270°-45° is northwest (NW); 45°-180° is east (E). Error bars not shown.

(Figure 11). While more variable, on average about 25% of {NO_y-NO_x} is HNO₃ in the NW and E surface wind sectors. Trainer *et al.* [1991] modeled the photochemical production of organic nitrates, such as butyl and isoprene nitrates, and predicted that these reactive N compounds may contribute as much as 1000 pptv to NO_y at night and 3000 pptv or more to NO_y midday. These high levels appear possible in light of the unusual results observed for several early evening hours between April 27 and 30, 1993. During these hours an air mass with easterly surface winds contained less than 1 ppbv of HNO₃, 4-5 ppbv of NO_x, and more than 8 ppbv of “unidentified” oxidized NO_y, presumably PAN and other organic nitrates (Figure 11).

5. Conclusions

Mean summertime HNO₃ mixing ratios at Harvard Forest agree well with results from other rural sites and fit in with the latitudinal HNO₃ gradient for the northeastern United States. This site receives air masses from both urban and rural source regions resulting in mean and median HNO₃ levels 4 times higher when surface winds were from the SW as opposed to the NW wind sector. High early morning HNO₃ and aerosol NO₃⁻ mixing ratios suggest of the entrainment of these species from aloft into the newly developing mixed layer. A behavior consistent with theories of nocturnal heterogeneous HNO₃ production in the “fossil” mixed layer.

The importance of acidic SO₄²⁻ aerosols in regulating the gaseous NH₃ levels at Harvard Forest is demonstrated by the low NH₃ mixing ratios and the exponential relationships between the NH₃/NH_x partitioning ratio and aerosol SO₄²⁻ concentrations. In the sulfate rich atmosphere above Harvard Forest, NH₃ mixing ratios appear to be suppressed below the NH₃ compensation point, suggesting that this N limited ecosystem may be losing N to the atmosphere through canopy NH₃ emissions. Air temperature is another factor controlling the NH₃ levels at this site. However, it is difficult to appor-

tion the controls on NH₃ between the temperature response of the NH₃ compensation point and the temperature sensitivity of NH₃/H₂SO₄ production. The temperature response of these two controls may have similar results with warmer temperatures perhaps resulting in both greater NH₃ canopy emissions and a larger NH₃/NH_x ratios for a given SO₄²⁻ concentration.

On average HNO₃ makes up about 20% of NO_y at midday. PAN and perhaps other organic nitrates are believed to make up a significant fraction of NO_y at Harvard Forest since the sum of the measured NO_y species (NO, NO₂, HNO₃, and aerosol NO₃⁻) typically account for between 60-80% of the summertime NO_y over the course of a day. HNO₃ makes up about half of the oxidized NO_y in polluted SW winds. However, unmeasured oxidized NO_y species comprise ~ 75% of the {NO_y-NO_x} in surface winds from the NW and E sectors, suggesting significant production of organic nitrates in these air masses.

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References

- Aneja, V.P., C.S. Clairborn, Z. Li, and A. Murthy, Trends, seasonal variations, and analysis of high-elevation surface nitric acid, ozone, and hydrogen peroxide, *Atmos. Environ.*, 28, 1781-1790, 1994a.

- Aneja, V.P., M. Das, D.-S. Kim, and B.E. Hartsell, Measurements and analysis of photochemical oxidants and trace gases in the rural troposphere of the southeast United States, *Is. J. Chem.*, **34**, 387-401, 1994b.
- Appel, B.R., and Y. Tokiwa, Atmospheric particulate nitrate sampling errors due to reactions with particulate and gaseous strong acids, *Atmos. Environ.*, **15**, 1087-1089, 1981.
- Appel, B.R., S.M. Wall, Y. Tokiwa, and M. Haik, Simultaneous nitric acid, particulate nitrate and acidity measurements in ambient air, *Atmos. Environ.*, **14**, 549-554, 1980.
- Appel, B.R., Y. Tokiwa, and M. Haik, Sampling of nitrates in ambient air, *Atmos. Environ.*, **15**, 283-289, 1981.
- Appel, B.R., Y. Tokiwa, E.L. Kothny, R. Wu, and V. Povard, Evaluation of procedures for measuring atmospheric nitric acid and ammonia, *Atmos. Environ.*, **22**, 1565-1573, 1988.
- Buhr, S.M., M.P. Buhr, F.C. Fehsenfeld, J.S. Holloway, U. Karst, R.B. Norton, D.D. Parrish, and R.E. Sievers, Development of a semi-continuous method for the measurement of nitric acid vapor and particulate nitrate and sulfate, *Atmos. Environ.*, **29**, 2609-2624, 1995.
- Cadle, S.H., R.J. Countess, and N.A. Kelly, Nitric acid and ammonia in urban and rural locations, *Atmos. Environ.*, **16**, 2501-2506, 1982.
- Clean Air Status and Trends Network (CASTNet) Database, Off. of Air and Radiat., U.S. Environ. Prot. Agency, Research Triangle Park, N.C., 1997.
- Clegg, S.L., P. Brimblecombe, and A.S. Wexler, Thermodynamic model of the system H⁺-NH₄⁺-SO₄²⁻-NO₃⁻-H₂O at tropospheric temperatures, *J. Phys. Chem.*, **102**, 2137-2154, 1998.
- Cofer, W.R. III, V.G. Collins, and R.T. Talbot, Improved aqueous scrubber for collection of soluble atmospheric trace gases, *Environ. Sci. Technol.*, **19**, 557-560, 1985.
- Crosley, D.R., Issues in the measurement of reactive nitrogen compounds in the atmosphere, *Rep. MP-94-035*, SRI Int., Menlo Park, Calif., March 1994.
- Davies, C.N., The entry of aerosols into sampling tubes and heads, *Br. J. Appl. Phys.*, **1**, 921-932, 1968.
- Davies, C.N., and M. Subari, Aspiration above wind velocity of aerosols with thin-walled nozzles facing at right angles to the wind direction, *J. Aeros. Sci.*, **13**, 59-71, 1982.
- Denmead, O.T., J.R. Freney, and J.R. Simpson, A closed ammonia cycle within a plant canopy, *Soil Biol. Biochem.*, **8**, 161-164, 1976.
- Dentener, F.J., and P.J. Crutzen, Reaction of N₂O₅ on tropospheric aerosols: Impact on the global distributions of NO_x, O₃ and OH, *J. Geophys. Res.*, **98**, 7149-7163, 1993.
- Edgerton, E.S., T.F. Lavery, and R.P. Boksleitner, Preliminary data from the USEPA dry deposition network: 1989, *Environ. Pollut.*, **75**, 145-156, 1992.
- Farquhar, G.D., P.M. Firth, R. Weselaar, and B. Weir, On the gaseous exchange of ammonia between leaves and the environment: Determination of the ammonia compensation point, *Plant Physiol.*, **66**, 710-714, 1980.
- Forrest, J., D.J. Spandau, R.L. Tanner, and L. Newman, Determination of atmospheric nitrate and nitric acid employing a diffusion denuder with a filter pack, *Atmos. Environ.*, **16**, 1473-1485, 1982.
- Georgopoulos, G.P., and J.H. Seinfeld, Statistical distribution of air pollutant concentrations, *Environ. Sci. Technol.*, **15**, 401A-416A, 1982.
- Goldstein, A.H., C.M. Spivakovsky, and S.C. Wofsy, Seasonal variations of nonmethane hydrocarbons in rural New England: Constraints on OH concentrations in northern latitudes, *J. Geophys. Res.*, **100**, 21,023-21,033, 1995.
- Goldstein, A.H., M.L. Goulden, H.W. Munger, S.C. Wofsy, and C.D. Geron, Season course of isoprene emissions from a midlatitude deciduous forest, *J. Geophys. Res.*, in press, 1998.
- Goulden, M.L., J.W. Munger, S.-M. Fan, B.C. Daube, and S.C. Wofsy, Exchange of carbon dioxide by a deciduous forest: Response to interannual climate variability, *Science*, **271**, 1576-1578, 1996.
- Gschwandtner, G., K. Gschwandtner, K. Eldridge, C. Mann, and D. Mobley, Historic emissions of sulfur and nitrogen oxides in the United States from 1900 to 1980, *J. Air Pollut. Control Assoc.*, **36**, 139-149, 1986.
- Hidy, G.M., Spatial and temporal distribution of airborne sulfate in parts of the U.S., *Atmos. Environ.*, **12**, 735-752, 1978.
- Keene, W.C. et al., An intercomparison of measurement systems for vapor and particulate phase concentrations of formic and acetic acids, *J. Geophys. Res.*, **94**, 6457-6472, 1989.
- Kelly, T.J., R.L. Tanner, L. Newman, P.J. Galvin, and J.A. Kadlecsek, Trace gas and aerosol measurements at a remote site in the northeast U.S., *Atmos. Environ.*, **18**, 2565-2576, 1984.
- Kleinman, L., et al., Ozone formation at a rural site in the southeastern United States, *J. Geophys. Res.*, **99**, 3469-3482, 1994.
- Klemm, O., and R.W. Talbot, A sensitive method for measuring atmospheric concentrations of sulfur dioxide, *J. Atmos. Chem.*, **13**, 325-342, 1991.
- Knoll, G.F., *Radiation Detection and Measurement*, 816 pp., John Wiley, New York, 1979.
- Langford, A.O., and F.C. Fehsenfeld, Natural vegetation as a source or sink for atmospheric ammonia: A case study, *Science*, **255**, 581-583, 1992.
- Langford, A.O., F.C. Fehsenfeld, J. Zachariassen, and D.S. Schimel, Gaseous ammonia fluxes and background concentrations in terrestrial ecosystems of the United States, *Global Biogeochem. Cycles*, **6**, 459-483, 1992.
- Lefer, B.L., The chemistry and dry deposition of atmospheric nitrogen at a rural site in the northeastern United States, Ph.D. thesis, 119 pp., Univ. of N.H., Durham, December 1997.
- Lefer, B.L., et al., Enhancement of acidic gases in biomass-burning impacted air masses over Canada, *J. Geophys. Res.*, **99**, 1721-1738, 1994.
- Lewin, E.E., R.G. DePena, and J.P. Shimshock, Atmospheric gas and particle measurements at a rural northeastern U. S. site, *Atmos. Environ.*, **20**, 59-70, 1986.
- Marti, J.J., A. Jefferson, X.P. Cai, C. Richert, P.H. McMurry, and F. Eisle, H₂SO₄ vapor pressure of sulfuric acid and ammonium sulfate solutions, *J. Geophys. Res.*, **102**, 3725-3735, 1997.
- Meyers, T.P., B.J. Huebert, and B.B. Hicks, HNO₃ deposition to a deciduous forest, *Boundary Layer Meteorol.*, **49**, 395-410, 1989.
- Meyers, T.P., B.B. Hicks, R.P.J. Hosker, J.D. Womack, and L.C. Satterfield, Dry deposition inferential measurement techniques--II. Seasonal and annual deposition rates of sulfur and nitrate, *Atmos. Environ.*, **25A** (10), 2361-2370, 1991.
- Moody, J.L., J.W. Munger, A.H. Goldstein, D.J. Jacob, and S.C. Wofsy, Harvard Forest regional-scale air mass composition by Patterns in Atmospheric Transport History (PATH), *J. Geophys. Res.*, **103**, 13,181-13,194, 1998.
- Moore, K.W., D.R. Fitzjarrald, R.K. Sakai, M.L. Goulden, J.W. Munger, and S.C. Wofsy, Seasonal variation in radiative and turbulent exchange at a deciduous forest in central Massachusetts, *J. Appl. Meteorol.*, **35**, 122-134, 1996.
- Munger, J.W., S.C. Wofsy, P.S. Bakwin, S.-M. Fan, M.L. Goulden, B.C. Daube, and A.H. Goldstein, Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a subarctic woodland; 1. Measurements and mechanisms, *J. Geophys. Res.*, **101**, 12,639-12,657, 1996.
- Munger, J.W., S.-M. Fan, P.S. Bakwin, M.L. Goulden, A.H. Goldstein, A.S. Colman, and S.C. Wofsy, Regional budgets for nitrogen oxides from continental sources: variations of rates for oxidation and deposition with season and distance from source regions, *J. Geophys. Res.*, **103**, 8355-8368, 1998.
- National Atmospheric Deposition Program, (NRSP-3)/National Trends Network, NADP/NTN Coord. Off., Nat. Resour. Ecol. Lab., Colorado State Univ., Fort Collins, February 17, 1997.
- Ollinger, S.V., J.D. Aber, G.M. Lovett, S.E. Millham, R.G. Lathrop, and J.M. Ellis, A spatial model of atmospheric deposition for the northeastern U.S., *Ecol. Appl.*, **3** (3), 459-472, 1993.
- Parrish, D.D., R.B. Norton, M.J. Bollinger, S.C. Liu, P.C. Murphy, D.L. Albritton, F.C. Fehsenfeld, and B.J. Huebert, Measurements of HNO₃ and NO₃ particulates at a rural site in the Colorado mountains, *J. Geophys. Res.*, **91**, 5379-5393, 1986.
- Parrish, D.D., M. Trainer, M.P. Buhr, B.A. Watkins, and F.C. Fehsenfeld, Carbon monoxide concentrations and their relation to concentrations of total reactive oxidized nitrogen at two rural U.S. sites, *J. Geophys. Res.*, **96**, 9309-9320, 1991.
- Parrish, D.D., et al., The total reactive oxidized nitrogen levels and the partitioning between the individual species at six rural sites in eastern North America, *J. Geophys. Res.*, **98**, 2927-2939, 1993.
- Peake, E., M.A. MacLean, and H.S. Sandhu, Total inorganic nitrate (particulate nitrate and nitric acid) observations in Calgary, Alberta, *J. Air Pollut. Control Assoc.*, **35**, 250-253, 1985.

- Peterson, B.J., and J.M. Melillo, The potential storage of carbon caused by eutrophication of the biosphere, *Tellus*, 37B, 117-127, 1985.
- Richards, L.W., Comments on the oxidation of NO₂ to nitrate: Day and night, *Atmos. Environ.*, 17, 397-402, 1983.
- Savoie, D.L., and J.M. Prospero, Particle size distribution of nitrate and sulfate in the marine atmosphere, *Geophys. Res. Lett.*, 9, 1207-1210, 1982.
- Schell, R.W., A historical perspective of atmospheric chemicals deposited on a mountain top peat bog in Pennsylvania, *Int. J. Coal Geol.*, 8, 147-173, 1987.
- Schindler, D.W., and S.E. Bayley, The biosphere as an increasing sink for atmospheric carbon: Estimates from increased nitrogen deposition, *Global Biogeochem. Cycles*, 7, 717-734, 1993.
- Schlesinger, W.H., and A.E. Hartley, A global budget for atmospheric NH₃, *Biogeochemistry*, 15, 191-211, 1992.
- Spicer, C.W., J.E. Howes, T.A. Bishop, L.H. Arnold, and R.K. Stevens, Nitric acid measurement methods: An intercomparison, *Atmos. Environ.*, 16, 1487-1500, 1982.
- Stecher, H.A. III, et al., Results of the Gas-Phase Sulfur Intercomparison Experiment (GASIE): Overview of experimental setup, results and general conclusions, *J. Geophys. Res.*, 102, 16,219-16,236, 1997.
- Stelson, A.W., and J.H. Seinfeld, Relative humidity and temperature dependence of the ammonium nitrate dissociation constant, *Atmos. Environ.*, 16, 983-992, 1982.
- Talbot, R.W., A.S. Vijgen, and R.C. Harriss, Measuring tropospheric HNO₃: Problems and prospects for nylon filter and mist chamber techniques, *J. Geophys. Res.*, 95, 7553-7561, 1990.
- Talbot, R.W., A.S. Vijgen, and R.C. Harriss, Soluble species in the Arctic summer troposphere: acidic gases, aerosols, and precipitation, *J. Geophys. Res.*, 97, 16,531-16,545, 1992.
- Talbot, R.W., et al., Large-scale distributions of tropospheric nitric, formic, and acetic acids over the western Pacific basin during wintertime, *J. Geophys. Res.*, 102, 28,303-28,313, 1997.
- Tang, I.N., On the equilibrium partial pressures of nitric acid and ammonia in the atmosphere, *Atmos. Environ.*, 14, 819-828, 1980.
- Tjepkema, J.D., R.C. Cartica, and H.F. Hemond, Atmospheric concentration of ammonia in Massachusetts and deposition on vegetation, *Nature*, 249, 445-446, 1981.
- Trainer, M., et al., Observations and modeling of the reactive nitrogen photochemistry at a rural site, *J. Geophys. Res.*, 96, 3045-3063, 1991.
- Williams, E.J., et al., An intercomparison of five ammonia measurement techniques, *J. Geophys. Res.*, 97, 11,591-11,611, 1992.
- Wofsy, S.C., M.L. Goulden, J.W. Munger, S.-M. Fan, P.S. Bakwin, B.C. Daube, S.L. Bassow, and F.A. Bazzaz, Net exchange of CO₂ in a mid-latitude forest, *Science*, 260, 1314-1317, 1993.
- Wolff, G.T., On the nature of nitrate in coarse continental aerosols, *Atmos. Environ.*, 18, 977-981, 1984.
- Wyers, G.P., R.P. Otjes, and J. Slanina, A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia, *Atmos. Environ.*, 27A, 2085-2090, 1993.

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