Regional budgets for nitrogen oxides from continental sources:
Variations of rates for oxidation and deposition with season
and distance from source regions

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Abstract. Measurements of nitrogen deposition and concentrations of NO, NO2, NOy (total oxidized N),
and O3 have been made at Harvard Forest in central Massachusetts since 1990 to
define the atmospheric budget for reactive N near a major source region. Total (wet plus dry)
reactive N deposition for the period 1990-1996 averaged 47 mmol m^-2 yr^-1 (126 μmol
m^-2 d^-1, 6.4 kg N ha^-1 yr^-1), with 34% contributed by dry deposition. Atmospheric input adds
about 12% to the N made available annually by mineralization in the forest soil. The corre-
sponding deposition rate at a distant site, Schefferville, Quebec, was 20 mmol m^-2 d^-1 during
summer 1990. Both heterogeneous and homogeneous reactions efficiently convert NOx to
HNO3 in the boundary layer. HNO3 is subsequently removed rapidly by either dry deposition
or precipitation. The characteristic (e-folding) time for NOx oxidation ranges from 0.30 days
in summer, when OH radical is abundant, to ~1.5 days in the winter, when heterogeneous re-
actions are dominant and O3 concentrations are lowest. The characteristic time for removal of
NOx oxidation products (defined as NO, minus NOx) from the boundary layer by wet and dry
deposition is ~1 day, except in winter when it decreases to 0.6 day. Biogenic hydrocarbons
contribute to N deposition through formation of organic nitrates but are also precursors of
reservoir species, such as peroxyacetylnitrate, that may be exported from the region. A simple
model assuming pseudo first-order rates for oxidation of NO, followed by deposition, pre-
dicts that 45% of NOx in the northeastern U.S. boundary layer is removed in 1 day during
summer and 27% is removed in winter. It takes 3.5 and 5 days for 95% removal in summer
and winter, respectively.

1. Introduction

Human activities have greatly increased the inputs of nitro-
gen oxides to the atmosphere (we define nitrogen oxides as
follows: NOx = NO + NO2, radicals that rapidly interconvert,
within minutes to hours; and NOy = NOx + NO3 + N2O5 +
HNO3 + peroxyacetylnitrate (PAN) + other organic nitrates +
aerosol nitrate, the family of radicals and nonradicals that in-
terconvert and are deposited on longer timescales i.e., hours
to days) [Davidson, 1991; Galloway et al., 1995; Logan,
1983; Prather et al., 1995]. Anthropogenic emissions of NO2
(mainly from combustion) exceed the natural inputs of fixed
nitrogen to the atmosphere in North America and other urban-
ized regions. Photochemical production of O3 in the tropo-
sphere is controlled by NOx radicals. Deposition of NOx
(along with NH3) contributes to nutrient loading and acidifi-
cation in sensitive ecosystems. Remote regions with low in-
puts from natural NO sources may be especially sensitive to
even small increases in reactive N because chemical and
ecological effects are nonlinear functions of concentration
[Liu et al., 1987; Wedin and Tilman, 1996]. The lifetime for
NOx removal determines the distance from the source region
over which N levels are perturbed from the natural back-
ground. Holland et al. [1997] note that uncertainties in pre-
dicted global distribution of nitrogen deposition lead to large
differences in estimates of global carbon uptake associated
with N fertilization.

Dentener and Crutzen [1993] noted the absence of a strong
seasonality in wet deposition of NO3 over Europe and North
America and argued that rates for production and removal of
HNO3 from the boundary layer are similar throughout the
year, with increased rates of HNO3 formation by heterogene-
ous hydrolysis of N2O5 in winter compensating for reduced
rates of homogeneous oxidation of NO2 by OH. However, the
contribution from dry deposition was not included, and sea-
sonal trends in wet deposition alone may be misleading. Total
annual nitrate deposition fluxes have been estimated at sites
in North America by inferring the dry deposition from aver-
average concentrations [Hanson and Lindberg, 1991; Johnson and Lindberg, 1992; Meyers et al., 1991], but long-term records of NOx and NOy concentrations and total (wet plus dry) nitrogen deposition fluxes have not been available to define seasonal cycles in the reactive nitrogen budget.

In 1990 we began continuous measurements of concentrations and eddy-covariance fluxes of NOx, concentrations of NOy and O3, and deposition of NO3' in precipitation at Harvard Forest in central Massachusetts. Additional measurements were made during the Arctic Boundary Layer Expedition (ABLE 3B) experiment in the summer of 1990 near Schefferville, Quebec. Munger et al. [1996] (hereinafter referred to as M96) demonstrated that NOy eddy fluxes can be reliably determined for extended periods by eddy-covariance measurements, identified horizontal and vertical transport and chemical reaction as dominant processes controlling dry deposition of NOy to the forest canopy, and noted the absence of stomatal influence on NOx dry deposition. In this paper we examine the seasonal trends in total nitrogen deposition, evaluate the mean lifetimes for oxidation of NO2 and deposition of NOx, in the boundary layer, and estimate the rate of nitrogen removal during transport from source regions for the period 1990 through 1996.

2. Site Description and Measurement Methods

Harvard Forest is located in Petersham, Massachusetts (42.53°N, 72.18°W), at an elevation of 340 m. Within 100 km the surroundings are largely rural with a mix of mostly small (population of ~10^4) and a few medium (population of ~10^5) towns surrounded by forests. Extensive urban areas with relatively high NOx emission densities lie within 200-500 km to the southwest of Harvard Forest (Figure 1). Average NOx emissions given in the National Acid Precipitation Assessment Program (NAPAP) inventory within 250 km of Harvard Forest are 214 μmol m^2 d^-1 [Environmental Protection Agency (EPA), 1989], ranging from 417 μmol m^2 d^-1 in the southwest quadrant, which includes the New York metropolitan area, to 75 μmol m^2 d^-1 in the mostly rural northwest quadrant. The Boston metropolitan area is 100 km to the east; however, the prevailing winds are westerly, and emissions from Boston rarely reach the site. Harvard Forest is similar in many respects to much of the northeastern United States outside the urban corridor along the coast.

The ABLE 3B tower site was located 13 km NW of Schefferville, Quebec, Canada (54.83°N, 66.67°W), at an elevation of 500 m. Observations were made from mid-June to mid-August 1990. Besides Schefferville (largely abandoned and being demolished) and a few small villages the nearest habitations were >200 kilometers away. Schefferville is hundreds of km from major NOx sources, except when forest fires are burning nearby; it represents a remote receptor site several days' transport time from major sources of NOx, in contrast to Harvard Forest, which is immediately adjacent to a major source region.

Concentrations of NO were measured by using O3 chemiluminescence. Concentrations of NO2 and NOy, respectively, were measured by using Xe-lamp photolysis and catalysis by hot Au with H2, to convert NO2 and NOy to NO. Dry-deposition fluxes of NOx were determined by eddy covariance. Concentrations of O3 at eight heights in the forest were determined by UV absorbance. Concentrations and fluxes of O3 above the canopy were determined by using a fast-response C2H4-chemiluminescent analyzer. Full details of the measurements are given by M96.

At both sites, precipitation was collected above the canopy in a polyethylene funnel that opened only during precipitation events. The sample drained to a fractionating collector housed in a refrigerator. Concentrations of NO3', SO42-, and Cl- were determined by ion chromatography. The analytical precision for rainwater analyses, determined from replicate analysis of samples and standards, was 2% or better. Additional data on precipitation composition at the National Atmospheric Deposition Program (NADP) Quabbin Reservoir site (42.392°N, 72.345°W) were obtained from the NADP data archive (http://nadp.nrel.colostate.edu/NADP/). National Atmospheric Deposition Program (NADP) Quabbin Reservoir site (42.392°N, 72.345°W) were obtained from the NADP data archive (http://nadp.nrel.colostate.edu/NADP/).
Deposition Program (NRSP-3)/National Trends Network, August, 1997, NADP/NTN Coord. Off., Ill. State Wat. Surv., Champaign, Ill., hereinafter referred to as NADP, 1997). Wet-deposition fluxes at Harvard Forest were corrected for missed samples or inefficient collection by multiplying the amount of precipitation recorded at a standard gauge located about 1 km from the tower (R. Lent, unpublished Harvard Forest data archives, 1997) by the volume-weighted average concentration for the event (for undersampled events) or by the monthly volume-weighted average (for missed events). Fresh and recently fallen snow-core samples were collected above polyethylene sheets set out at several locations within \(-50\) m radius prior to a snow event. At Schefferville, rain volumes collected by the fractionating collector were used to compute rainfall amounts because rainfall in the area was topographically influenced [Fitzjarrald and Moore, 1994] and the nearest standard rain gauge was some distance away. Collection efficiency for light misting rains accompanied by winds may be less than 100% for the precipitation funnel. When rain was reported at the site, but sample was partially lost (spill or depth for the rain gauge network [Fitzjarrald and Moore, 1994] was used.

3. Results

3.1. Sampling Statistics

Inevitably, long-term data sets are incomplete, and the simple sum of all the data does not provide total flux over the sampling interval. Gaps occur as a result of routine instrument calibrations, periodic shutdowns, sensor malfunctions, and other problems (e.g., lightning strikes, and power failures). Individual observations may not be truly independent. Diel variations, synoptic patterns, and seasonal trends introduce autocorrelation into the data. For example, the lagged correlation of mean midday NO\(_x\) eddy fluxes is 0.25 for a 1 day lag and exceeds 0.1 for lags up to 40 days. These correlations must be properly accounted for in filling data gaps and aggregating the data to monthly, seasonal, and annual timescales [Goulden et al., 1996a].

Hourly observations of NO\(_x\) eddy flux consist of a central population that fits a lognormal distribution with some low outliers, as illustrated by the July data from Harvard Forest (Figure 2,top). Other time periods show similar patterns but with different ranges and median values. Integrated daily fluxes at Harvard Forest for each month (illustrated for July) and for Schefferville also fit a lognormal distribution over the central portion of their range (Figure 2, bottom). NO\(_x\) eddy fluxes had a mean diel cycle with a morning maximum (M96); the period 1000 to 1200 contributed nearly 20% of the integrated daily eddy flux. We have aggregated the data in monthly increments, consistent with observed autocorrelation, to provide a sufficient number of observations from each hour of the day to obtain accurate means and still resolve seasonal variations. Means are computed independently for each hour of the day, and the mean diel cycle is summed to give mean daily flux for each month. The median or geometric mean represents the central tendency of lognormally distributed data. However, we use the arithmetic mean here because it incorporates important contributions from infrequent high-deposition events that may provide a significant fraction of total deposition during an averaging interval.

Half the NO\(_x\) eddy flux input at Schefferville, and during the summers at Harvard Forest, was deposited in extreme events on 25% and 20% of the days, respectively. Increasing skewness and contribution from rare events leads to greater potential for sampling error from missed data. We therefore examined the uncertainty associated with missing data by generating random subsamples of the data. The means (or medians) of subsamples containing \(\geq 50\%\) of the data vary by 10-15%. Variability increases sharply as more data are excluded (Figure 3). We estimated the uncertainty of the NO\(_x\) eddy-flux totals by computing the standard deviation of random subsamples that include 50% of the data from each interval.

On account of the smaller sample size for Schefferville data, individual days were integrated separately. Missing data were interpolated between adjacent points; days with fewer than 20 hours of valid data were rejected, and daily totals were computed. These values were used to obtain a seasonal mean, and estimates of the sampling uncertainty were derived from the standard deviation of data from valid days.

3.2. Combined Deposition

3.2.1. Harvard Forest. Monthly average concentrations of NO\(_3^-\) in rainwater at Harvard Forest (Figure 4,top) compared closely with the long-term means for rain sampled at the nearby NADP Quabbin reservoir site, implying that precipitation collected at Harvard Forest is regionally representative. The annual volume-weighted mean concentration of NO\(_3^-\) at Harvard Forest was 25 \(\mu\)mol l\(^{-1}\), with a minimum of \(-20 \mu\)mol l\(^{-1}\) in fall and winter and a maximum of 30 \(\mu\)mol l\(^{-1}\) in early summer. Daily inputs of NO\(_3^-\) by precipitation ranged from \(<1 \mu\)mol m\(^2\) d\(^{-1}\) for a trace of rain to \(>2000 \mu\)mol m\(^2\) d\(^{-1}\)

![Figure 2](image_url).
for a particularly dirty (NO$_3^-$ = 100 µmol l$^{-1}$) large event. The distribution of wet-deposition data at Harvard Forest was highly skewed; 13% of the events with largest inputs contributed half the wet deposition of NO$_3^-$, a more significant influence of extreme events than that for dry deposition. Wet deposition of NO$_3^-$ (Figure 4, bottom) peaked in summer at Harvard Forest, as observed at Quabbin Reservoir and other NADP sites in the northeastern United States (NADP, 1997).

Daily integrated NO$_y$ eddy fluxes measured by eddy covariance ranged from near 0 to 470 µmol m$^{-2}$ d$^{-1}$. Mean daily dry-deposition fluxes of NO$_y$ at Harvard Forest for monthly intervals generally showed low values in winter and higher values in summer or fall (Figure 5). The integrated daily NO$_y$ eddy fluxes show seasonal differences that were not observed in the midday mean eddy fluxes because of day length differences and the strong diel cycle in NO$_y$ eddy fluxes during summer months (M96). Monthly deposition (wet plus dry) of reactive N for the 7 years beginning January 1, 1990 (Figure 6) exhibited values of around 200 µmol m$^{-2}$ d$^{-1}$ during the growing seasons of all years except 1995, which had an exceptional drought. Eddy fluxes (dry deposition) of N during the summer of 1990 were higher, and nitrate wet deposition was lower than that in subsequent years. Unusual meteorological conditions may be responsible, but possible artifacts from a change in the NO$_y$ catalyst (M96) cannot be ruled out. Nevertheless, conclusions drawn from the 7-year data set are not significantly different from the 6-year data set excluding 1990. Variations in wet inputs tended to compensate for changes in dry deposition. The decline in dry deposition during 1994 (Figure 5) was offset by increased wet deposition, and the total deposition (Figure 6) was comparable to previous years. However, reduced wet deposition during a severe drought in summer 1995 was not offset by increased...
dry deposition. Total NO\textsubscript{3} inputs on an annual basis, averaged 47 ± 7.4 (sum of monthly means plus or minus monthly standard deviation) mmol m\textsuperscript{-2} yr\textsuperscript{-1} (Figure 7) with 34% contributed by dry deposition. Total reactive N deposition was highest in summer and early fall (4-5 mmol m\textsuperscript{-2} month\textsuperscript{-1}; 150 µmol m\textsuperscript{-2} d\textsuperscript{-1}) and decreased by about a factor of 2 in winter months. Peak deposition rates coincide with highest fraction of NO\textsubscript{x} oxidation products (minima in NO\textsubscript{x}:NO\textsubscript{y}) and not with the maximum NO\textsubscript{x} concentrations, which are highest in winter (M96).

3.2.2. Schefferville. The overall volume-weighted NO\textsubscript{3}\textsuperscript{-} concentration in rainwater at the Schefferville tower site was 3.8 µmol l\textsuperscript{-1}, roughly a factor of 10 less than that at Harvard Forest in summer. Nitrate deposition in rainwater varied from 0.4 µmol m\textsuperscript{-2} d\textsuperscript{-1} to 120 µmol m\textsuperscript{-2} d\textsuperscript{-1}, with a mean and median of 15 and 7 µmol m\textsuperscript{-2} d\textsuperscript{-1}, respectively. Seven days (14%) of a total of 50 rainy days accounted for 50% of the NO\textsubscript{3}\textsuperscript{-} wet deposition, indicating that sporadic advection of pollutants was very important. A single event with ~10 µmol l\textsuperscript{-1} [NO\textsubscript{3}\textsuperscript{-}] on July 30, which has been identified as an anthropogenic pollution event [Bakwin et al., 1994], contributed 17% of the wet deposition during the period.

Integrated daily NO\textsubscript{y} eddy fluxes were 0.7-37 µmol m\textsuperscript{-2} d\textsuperscript{-1} (M96, Figure 5), with a mean and median of 7.6 and 6.4 µmol m\textsuperscript{-2} d\textsuperscript{-1}, respectively. Dry-deposition fluxes of nitrate were more uniform than wet-deposition fluxes; daily totals exceeded 14 µmol m\textsuperscript{-2} d\textsuperscript{-1} on only 4 days (Figure 8). Total NO\textsubscript{y} inputs ranged from <5 to 130 µmol m\textsuperscript{-2} d\textsuperscript{-1}, with a mean value of 18.5 µmol m\textsuperscript{-2} d\textsuperscript{-1} (0.55 mmol m\textsuperscript{-2} month\textsuperscript{-1}), about 12% of the deposition rate at Harvard Forest during summer. Dry deposition contributed 41% of the total reactive N deposition at the Schefferville site, compared to 77% during the same period at Harvard Forest. On average, however, dry deposition contributed 35% of the total reactive N deposited during summer at Harvard Forest.

3.3. Regional Comparisons

Deposition rates for N determined at 20 northeastern U.S. sites in the National Dry Deposition Network (NDDN) and the Integrated Forest Study (IFS) ranged from 24 to 68 mmol m\textsuperscript{-2} yr\textsuperscript{-1} (mean 43) [Johnson and Lindberg, 1992; Meyers et al., 1991]. The deposition rates determined in these studies by inferential method are consistent with the eddy-covariance measurements at Harvard Forest. Estimated contributions from dry deposition at IFS and NDDN sites fell in the range 30-70%, which is comparable to results of direct measurements from Harvard Forest and Schefferville. Nitrogen deposition fluxes at Harvard Forest were intermediate between deposition at West Point, New York (56 mmol m\textsuperscript{-2} yr\textsuperscript{-1}) and Howland, Maine (34 mmol m\textsuperscript{-2} yr\textsuperscript{-1}), consistent with the
southwest-to-northeast decline in N deposition across the region noted by Ollinger et al. [1993]. No clear seasonal cycle in total N deposition was apparent across the NDDN [Meyers et al., 1991], although the West Point site in New York had a summer maximum during 2 of 3 years studied. The seasonal trends at Harvard Forest become most apparent when many years of data are aggregated; this finding illustrates the value of long-term data sets in identifying underlying patterns that may be masked by atmospheric variability (e.g. wet summer in 1991 and dry summer in 1990).

3.4. Ammonium Inputs

Reduced nitrogen in the form of NH₃ and NH₄⁺ in precipitation and dry deposition also contributes biologically available N. We did not measure NH₄⁺ in precipitation at Harvard Forest, but we can estimate it from the measured SO₄²⁻ inputs at Harvard Forest and mean NH₄⁺:SO₄²⁻ ratio in precipitation collected at the Quabbin Reservoir NADP site (NADP, 1997) (Figure 9). Estimated wet deposition of NH₄⁺ (8.1 mmol m⁻² yr⁻¹) was ∼15% of the total NO₃⁻ input at Harvard Forest. Tjeckema et al. [1981] observed low concentrations and deposition of NH₃ at Harvard Forest and estimated that aerosol deposition of NH₄⁺ added 4.3 mmol m⁻² yr⁻¹. Recent measurements [Lefer, 1997] (B.L. Lefer et al., Nitric acid and ammonia at a rural northeastern U.S. site, submitted to Journal of Geophysical Research, 1997) confirm that NH₃ levels are low at Harvard Forest.

4. Discussion

4.1. Atmospheric Contribution to Ecosystem Nitrogen Pools

Atmospheric N deposition at Harvard Forest is significant in comparison with the N turnover by vegetation but small in relation to the total N content of vegetation and soils. Total N in the near-surface soil (5410 mmol m⁻²) at a nearby hardwood stand [Aber et al., 1993] represents about 90 years accumulation at present rates for nitrate plus ammonium deposition (60.4 mmol N m⁻² yr⁻¹). Combined input of atmospheric nitrate and ammonium also appears small (∼12%) in comparison with the annual net N mineralization rate of 500 mmol m⁻² yr⁻¹ [Aber et al., 1993]. If atmospheric inputs of N are distributed uniformly within these pools, deposition may have only small effects on the ecosystem, although long-term cumulative effects might be important [Wedin and Tilman, 1996]. However, atmospheric inputs of N are roughly half the green foliar N content (100-150 mmol m⁻²) and nearly equal to the N deposited in litter (60-70 mmol m⁻² yr⁻¹). Foliar absorption of N could lead to more significant effects by...
Table 1. Quarterly Statistics for N deposition and Meteorological Conditions at Harvard Forest

<table>
<thead>
<tr>
<th>Season</th>
<th>Year</th>
<th>Total N Deposition, µmol m⁻² d⁻¹</th>
<th>Frequency of Surface Winds by Sector</th>
<th>Frequency of Rainfall, %</th>
<th>Rainfall amount, mm</th>
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* We define the seasons as follows: winter is December through February, spring is March through May, summer is June through August, and fall is September through November.

4.2. Meteorological and Seasonal Factors

Nitrogen deposition measured at Harvard Forest depends on wind patterns that control transport from source regions, frequency and amount of precipitation, oxidizing capacity of the atmosphere, and other factors. Mean NO₂ concentrations and eddy fluxes were higher for periods with southwesterly winds, the direction associated with transport from east coast urban areas, and with trajectories originating in the Great Lakes/Ohio Valley region [Moody et al., 1998] (see Table 1). Periods with frequent wet weather or above average rainfall amounts are also associated with enhanced N deposition. A least-squares fit to a linear model of the data that predicts N deposition by season, the percentage of winds from the SW sector, and the frequency of rainfall gave a multiple R² of 0.65 (see Table 2a). The regression model identifies a significant (p< 0.01) seasonal component with an amplitude of 40 µmol m⁻² d⁻¹ (Table 2b) accounting for 38% of the variance in the data. The variations in N deposition due to differences in frequency of SW wind and precipitation account for an additional 17% and 11% of variance, respectively. Each of the estimated effects for the observed range of SW wind and precipitation frequency is about 30 µmol m⁻² d⁻¹. We attribute the influence of wind direction to advection from source regions and the influence of precipitation frequency on scavenging processes. We argue below that the seasonal dependence of NO₂ deposition is due to differences in chemical processing.

4.3. Influence of Rates for Oxidation of NO₂ on NOy Deposition Flux

4.3.1. Estimated HNO₃ production rates. As M96 noted, direct deposition of NO₂ is a small contribution to the dry deposition of NO₂, HNO₃ and organic nitrates (see below) account for NO₂ dry deposition. Aerosol nitrate and HNO₃ are the sources of nitrate in precipitation. In this section we evaluate the seasonal pattern of production rates for depositing species, HNO₃ and organic nitrates that can be derived from the observed concentrations at Harvard Forest, and compare it with the observed deposition rates. We will consider two inorganic pathways for production of HNO₃: homogeneous oxidation of NO₂,

\[
NO₂ + OH \rightarrow HNO₃, \quad (1)
\]

and heterogeneous oxidation, via reactions (2)-(4), culminating in hydrolysis of N₂O₅ on aerosol surfaces. Photolysis, reaction (5), terminates this pathway.
Although the detailed chemistry of hydroxyalkyl nitrates has not been worked out, atmospheric models that include them assume they have a deposition velocity and rainfall scavenging efficiency equal to that of HNO$_3$ [Horowitz et al., 1998; Liang et al., 1998; Trainer et al., 1991]. Production of hydroxyalkyl nitrates is examined here in order to evaluate this assumption.

We compute the mean and variance of potential HNO$_3$ production rates in the regional boundary layer surrounding Harvard Forest, using distributions of precursor concentrations for each month defined by means and logarithmic standard deviations of midday data (Table 3). We use surface measurements during the middle of the day, when vertical mixing is most intense, as the most representative of concentrations throughout the mixed layer. We exclude the high and low extremes (data outside the 12.5 and 87.5 percentiles) that occur in conditions that may not be regionally representative. Temperatures in the mixed layer are adjusted from the surface observations by a 6°C km$^{-1}$ lapse rate. Regionally representative mixed-layer depths are taken from Holzworth [1967] to account for seasonal variation in mixing heights. Concentrations and temperature-adjusted rate constants [DeMore et al., 1997] are applied to equations for the rate-limiting reaction in each pathway to yield a set of rates for HNO$_3$ production.

The homogeneous production of HNO$_3$ on a 24-hour average basis is given by $\kappa_1[\text{OH}]$, where $[\text{OH}]$ is the 24-hour average OH concentration from a three-dimensional chemical tracer model [Wang et al., 1998] that includes detailed NO$_x$ and hydrocarbon chemistry. The predicted OH seasonal cycle has an amplitude consistent with seasonal variations in hydrocarbon concentrations at Harvard Forest [Goldstein et al., 1995]. The resulting production rates depend on seasonal variation in ambient NO$_x$ and OH concentrations.

We assume that heterogeneous formation of HNO$_3$ is limited by reaction (2) forming NO$_3$. For typical particle concentrations in the continental boundary layer and a sticking coefficient, $\chi = 0.1$ [DeMore et al., 1997], the lifetime of NO$_2$ is shorter than the duration of night. Dentener and Crutzen [1993] computed the annual zonal mean lifetime for NO$_2$ as <1 hour in northern midlatitudes below 850 mbar, due primarily to SO$_4^{2-}$ aerosol from anthropogenic sources. The reaction probability for NO$_3$ with aerosol surfaces in the continental boundary layer is 2 orders of magnitude less than that of N$_2$O$_5$ [Rudich et al., 1996]. The rate for heterogeneous formation of HNO$_3$ from hydrolysis of N$_2$O$_5$ is given by $2 \times J_{\text{phot}} [\text{NO}_3][\text{N}_2\text{O}_5]dt$. Because NO is fully oxidized to NO$_2$ at night, we initialize nighttime mixed-layer NO$_2$ concentrations with midday NO$_x$ (NO + NO$_2$) and allow NO$_2$ to decay exponentially over time (NO$_2$ = NO$_x$ (0) exp(-k$_2$O$_3$)). Fresh emis-

**Table 2a. Regression Results for the Linear Model fit of N Deposition Predicted by Seasonality and Frequency of Precipitation**

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Degrees of Freedom</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>Pr(F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Season</td>
<td>3</td>
<td>12,930</td>
<td>4,311.0</td>
<td>0.002</td>
</tr>
<tr>
<td>SW winds</td>
<td>1</td>
<td>5,930</td>
<td>5,930.0</td>
<td>0.006</td>
</tr>
<tr>
<td>Frequency of precipitation</td>
<td>1</td>
<td>3,597</td>
<td>3,597.0</td>
<td>0.026</td>
</tr>
<tr>
<td>Residual</td>
<td>19</td>
<td>11,700</td>
<td>615.7</td>
<td></td>
</tr>
</tbody>
</table>

Regression coefficients$^b$

- Intercept ($a_0$) $\mu$mol m$^{-2}$ d$^{-1}$: 129, 5.0
- Season 1, $\mu$mol m$^{-2}$ d$^{-1}$: -8, 9.2
- Season 2, $\mu$mol m$^{-2}$ d$^{-1}$: 16, 8.6
- Season 3, $\mu$mol m$^{-2}$ d$^{-1}$: 16, 10.0
- SW winds, $\mu$mol m$^{-2}$ d$^{-1}$: 2.0, 1.1
- Frequency of Precipitation, $\mu$mol m$^{-2}$ d$^{-1}$: 1.5, 0.6

We assume that heterogeneous formation of HNO$_3$ is limited by reaction (2) forming NO$_3$. For typical particle concentrations in the continental boundary layer and a sticking coefficient, $\chi = 0.1$ [DeMore et al., 1997], the lifetime of NO$_2$ is shorter than the duration of night. Dentener and Crutzen [1993] computed the annual zonal mean lifetime for NO$_2$ as <1 hour in northern midlatitudes below 850 mbar, due primarily to SO$_4^{2-}$ aerosol from anthropogenic sources. The reaction probability for NO$_3$ with aerosol surfaces in the continental boundary layer is 2 orders of magnitude less than that of N$_2$O$_5$ [Rudich et al., 1996]. The rate for heterogeneous formation of HNO$_3$ from hydrolysis of N$_2$O$_5$ is given by $2 \times J_{\text{phot}} [\text{NO}_3][\text{N}_2\text{O}_5]dt$. Because NO is fully oxidized to NO$_2$ at night, we initialize nighttime mixed-layer NO$_2$ concentrations with midday NO$_x$ (NO + NO$_2$) and allow NO$_2$ to decay exponentially over time (NO$_2$ = NO$_x$ (0) exp(-k$_2$O$_3$)). Fresh emis-

**Table 2b. Mean Annual Cycle for N Deposition at Harvard Forest Derived From Seasonal Factors**

<table>
<thead>
<tr>
<th>Season</th>
<th>Deviation from annual mean$^a$, $\mu$mol m$^{-2}$ d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>16</td>
</tr>
<tr>
<td>Summer</td>
<td>16</td>
</tr>
<tr>
<td>Fall</td>
<td>-8</td>
</tr>
<tr>
<td>Winter</td>
<td>-24</td>
</tr>
</tbody>
</table>

$^a$The value for the fourth season is set by the requirement that the seasonal cycle sum to zero.
Production of hydroxyalkyl nitrates begins in June and is activated NO\textsubscript{x} and O\textsubscript{3}, with much slower rates at other times. Oxidation should occur during pollution episodes with elevated NO\textsubscript{3} and O\textsubscript{3}, but lower O\textsubscript{3} concentrations and colder temperatures reduce rates for formation of NO\textsubscript{3}. Note that the variability for estimated heterogeneous HNO\textsubscript{3} production is greatest in the spring and fall months as well. Rapid NO\textsubscript{x} oxidation should occur during pollution episodes with elevated NO\textsubscript{2} and O\textsubscript{3}, with much slower rates at other times. Production of hydroxyalkyl nitrates begins in June and reaches a maximum in July and August that is comparable to the inorganic HNO\textsubscript{3} production terms (Figure 10, bottom panel).

Computed rates for heterogeneous and homogeneous HNO\textsubscript{3} production roughly balance the mean deposition rate observed at Harvard Forest during winter and fall (Figure 11). In summer, however, inorganic production of HNO\textsubscript{3} does not balance the observed deposition. Concentration profiles at Harvard Forest are not consistent with NO\textsubscript{x} having a large deposition velocity (M96), but even a deposition velocity of 1 cm s\textsuperscript{-1} would not account for the imbalance because NO\textsubscript{x} concentrations are too small. The apparent deficit in NO\textsubscript{x} oxidation during the growing season points to a mechanism linked to vegetation. The seasonality of hydroxyalkyl nitrate formation roughly matches the apparent excess in N deposition. However, its absolute magnitude is less certain, because mean hydrocarbon fluxes for the region must be estimated, and the complete chemical mechanism for this series of reactions has not been determined. Terpene emissions may be relatively more important in the spring and fall when conifers are active but oaks are dormant. The magnitude of hydroxyalkyl nitrate-mediated NO\textsubscript{x} oxidation that we estimate for the northeastern United States is in agreement with model predictions that this process accounts for 25% of the NO\textsubscript{x} deposition in North America during summer (Liang et al., 1997).

At the remote site, near Schefferville, computed local production of HNO\textsubscript{3} is 2.2 \textmu mol m\textsuperscript{-2} d\textsuperscript{-1} in summer, only about 10% of the observed average deposition, 20 \textmu mol m\textsuperscript{-2} d\textsuperscript{-1}, but comparable to the minimum observed deposition (Figure 8). We noted previously that a few episodes accounted for a large proportion of the total N deposition at Schefferville, such as the rain event on July 30 and the elevated dry deposition on July 1-5 (Figure 8). Bakwin et al. (1994) attributed these events to advection of pollutants associated with passage of high-pressure systems that import depositing species of NO\textsubscript{x} from urban-industrial centers.

### 4.3.2. Characteristic times for NO\textsubscript{x} oxidation and deposition
We can directly estimate the time constants, \( \tau \), for NO\textsubscript{x} oxidation by setting the concentrations of O\textsubscript{3} and OH to

<table>
<thead>
<tr>
<th>Month</th>
<th>NO\textsubscript{x} Deposit, \mu mol m\textsuperscript{-2} d\textsuperscript{-1}</th>
<th>Geometric Mean, pptv</th>
<th>Geometric Mean, pptv</th>
<th>Geometric Mean, pptv</th>
<th>Arithmetic Mean, ppbv</th>
<th>s.d., ppbv</th>
<th>OH\textsuperscript{b}, 10\textsuperscript{6} molecules cm\textsuperscript{-2}, T, °C</th>
<th>Mixing Height, m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan.</td>
<td>94.8</td>
<td>5254</td>
<td>0.51</td>
<td>3279</td>
<td>0.55</td>
<td>2688</td>
<td>0.58</td>
<td>27</td>
</tr>
<tr>
<td>Feb.</td>
<td>91.3</td>
<td>6158</td>
<td>0.4</td>
<td>2796</td>
<td>0.56</td>
<td>2162</td>
<td>0.59</td>
<td>34</td>
</tr>
<tr>
<td>March</td>
<td>121.9</td>
<td>5095</td>
<td>0.38</td>
<td>2110</td>
<td>0.5</td>
<td>1657</td>
<td>0.53</td>
<td>41</td>
</tr>
<tr>
<td>April</td>
<td>139.4</td>
<td>3898</td>
<td>0.38</td>
<td>1282</td>
<td>0.54</td>
<td>1023</td>
<td>0.57</td>
<td>45</td>
</tr>
<tr>
<td>May</td>
<td>159.4</td>
<td>3402</td>
<td>0.33</td>
<td>903</td>
<td>0.39</td>
<td>740</td>
<td>0.41</td>
<td>45</td>
</tr>
<tr>
<td>June</td>
<td>128.2</td>
<td>2918</td>
<td>0.32</td>
<td>703</td>
<td>0.22</td>
<td>604</td>
<td>0.23</td>
<td>46</td>
</tr>
<tr>
<td>July</td>
<td>183.7</td>
<td>3073</td>
<td>0.35</td>
<td>677</td>
<td>0.24</td>
<td>558</td>
<td>0.27</td>
<td>46</td>
</tr>
<tr>
<td>Aug.</td>
<td>169.6</td>
<td>3547</td>
<td>0.33</td>
<td>772</td>
<td>0.34</td>
<td>661</td>
<td>0.35</td>
<td>44</td>
</tr>
<tr>
<td>Sept.</td>
<td>131.9</td>
<td>3513</td>
<td>0.39</td>
<td>1138</td>
<td>0.44</td>
<td>920</td>
<td>0.47</td>
<td>35</td>
</tr>
<tr>
<td>Oct.</td>
<td>122</td>
<td>5075</td>
<td>0.43</td>
<td>1979</td>
<td>0.52</td>
<td>1666</td>
<td>0.53</td>
<td>32</td>
</tr>
<tr>
<td>Nov.</td>
<td>108.8</td>
<td>6737</td>
<td>0.43</td>
<td>3535</td>
<td>0.48</td>
<td>2974</td>
<td>0.5</td>
<td>27</td>
</tr>
<tr>
<td>Dec.</td>
<td>107.8</td>
<td>5658</td>
<td>0.52</td>
<td>3226</td>
<td>0.49</td>
<td>2739</td>
<td>0.5</td>
<td>26</td>
</tr>
</tbody>
</table>

Means and standard deviations for the concentrations are computed from the central 50% of the data for each month.

* Standard deviation of log-transformed data.

OH concentrations from Wang et al. [1998].

Mixed-layer height from Holzworth, [1967].
Figure 10. Computed production of HNO$_3$ by (top) NO$_2$ + OH and (middle) NO$_2$ + O$_3$ reactions for observed concentrations of NO$_x$, NO$_2$, O$_3$, and air temperatures at Harvard Forest and typical values of OH and mixed layer depths in the northeastern United States. For each month, 1000 individual estimates of HNO$_3$ production were generated by using random values of concentrations picked from data distributions as defined in Table 3. The solid lines with solid circles indicate medians; open circles are the mean values. Long-dashed lines bound the twenty-fifth and seventy-fifth percentiles of the computed values; short-dashed lines are the standard deviations. (bottom) Potential production of hydroxyalkyl nitrates for the observed isoprene emission flux at Harvard Forest (solid line) and the production rate if the isoprene fluxes were a factor of 2 less (dashed line). Corresponding production rates at Schefferville are 1.6 and 0.6 μmol m$^{-2}$ d$^{-1}$ for homogeneous and heterogeneous pathways, respectively.

Figure 11. Total production of HNO$_3$ by homogeneous (dark shading), heterogeneous (light shading), and hydroxyalkyl nitrate (stippled) pathways in the mixed layer as estimated in Figure 10 versus observed N deposition (solid line) at Harvard Forest. Uncertainty estimates for the production and deposition terms (Figures 7 and 10) are omitted for clarity.
for oxidation by OH and O₃. The characteristic time for deposition of NOₓ - NO₃ at Schefferville, 0.76 day, is slightly less than that at Harvard Forest.

Figure 12 shows that removal of NOₓ oxidation products (NOₓ - NO₃) takes slightly longer than their production for most of the year. Hence, within the region surrounding Harvard Forest, NOₓ oxidation products tend to build up in relation to the total reactive N concentration. Relatively long lifetimes for deposition are consistent with the observation that some HNO₃ remains when an air parcel reaches a remote area such as Schefferville, where local oxidation of ambient NOₓ accounts for only 10% of NOₓ deposition. Because NOₓ oxidation is so rapid, the NOₓ observed at Schefferville is likely to arise from decomposition of PAN or other long-lived species transported there, rather than as NOₓ [Fan et al., 1994]. Thus the fraction of NOₓ converted to stable organics is critical for supplying reactive N to the remote troposphere. Our results imply that, at Schefferville, NOₓ is provided by decomposition of reservoir species such as PAN [Singh and Hanst, 1981] and that PAN also supports background levels of NOₓ. Episodic transport of HNO₃ and other nonradical species accounts for high levels of NOₓ and pulses of N deposition.

Figure 12. (top) Characteristic (e-folding) times for HNO₃ production estimated from modeled OH concentrations, monthly mean observed O₃ concentrations, and isoprene fluxes. (bottom) Deposition lifetimes for NOₓ (open circles) and for NOₓ oxidation products, NOₓ = NOₓ - NO₃ (solid squares) are determined from the observed deposition flux and column mass. The overall chemical lifetime is the combination of characteristic times for reaction with OH, O₃, and isoprene (dashed line with open triangles). The characteristic times for OH and O₃ oxidation (top) and the overall chemistry and deposition lifetimes (bottom) at Schefferville in summer are indicated by symbols on the right margin (OH, O₃, R, D).

4.3.3. NOₓ budget integration. From the differential equations for rates of NOₓ oxidation and deposition (dNOₓ = -kₓNOₓdt, and dHNO₃ = (kₓNOₓ - kₙHNO₃)dt, respectively) we can derive a simple expression to predict the concentration of HNO₃ in the boundary layer downwind of a major source region,

\[ HNO₃(t) = \frac{NOₓ(0)}{D} \left( \frac{kₙ}{(kₓ - kₙ)} \right) (e^{-kₓt} - e^{-kₙt}) \]  

Here HNO₃(t) is the concentration of HNO₃ (and other rapidly deposited compounds) at time after emission, t, NOₓ(0) is the initial concentration of NOₓ at the emission source, and kₓ and kₙ are effective first-order rate constants (derived from photochemical calculations and from observations) for photochemical production and deposition, respectively. Note that kₓ reflects heterogeneous, homogeneous, and organic pathways for conversion of NOₓ to HNO₃ (or other rapidly depositing species) and kₙ accounts for total (wet plus dry) deposition. We include a dilution factor, D, to account for mixing of the polluted air parcel with cleaner background air (D cancels out of the analysis of ratios of species).

This ultra-simple model allows us to assess the fraction of NOₓ deposited in the region and the extent of the receptor area, using fluxes and concentrations of NOₓ observed at a single station. The model illustrates the consequences of seasonal trends in reaction and deposition rates and provides a first estimate for the fraction exported. We use mean concentrations and rates for chemical reactions and deposition, and
Figure 13. (top) Values of the NO_x ratio, NO/(NO_x + HNO_3), (middle) HNO_3 fraction, f_{HNO_3} = HNO_3(t)/(NO_x(0)/D), and (bottom) fraction of NO_x that has been deposited, computed from equation (6) (see text) by using seasonal mean values of reaction and deposition time constants (in days) for chemical reaction (τ_d) and deposition (τ_c) taken from Figure 12.

The product of k_d × f_{HNO_3} defines the fraction of initial NO_x deposited in unit time at travel time t downwind, where f_{HNO_3} is the fraction of odd nitrogen present as HNO_3 relative to the initial NO_x (f_{HNO_3} = HNO_3(t)/(NO_x(0)/D) = 1/(k_d - k_c) (e^{-k_d t} - e^{-k_c t}). The value of f_{HNO_3} is zero at the emission source (t=0), increases downwind to a maximum, and then gradually declines to 0 as NO_x is oxidized and deposited (Figure 13, middle). Note that because the parcel is dispersing with time, concentrations and deposition per unit area typically decline with increasing distance from the source. For summer conditions the peak in f_{HNO_3} occurs at ages of <1 day, while for winter conditions with slower chemistry the peak is delayed and broadened such that f_{HNO_3} in winter exceeds the summer values for parcel ages of >2 days.

Integration of k_d × f_{HNO_3} over time gives the cumulative fraction of NO_x deposited (Figure 13, bottom): 45% for t = 1 day in summer, 27% in winter. The time required to remove 95% of NO_x is 3.5 days in summer and 5 days in winter. This analysis indicates that transport and dispersion of NO_x in the boundary layer cannot account for most of the atmospheric N in the remote troposphere, because oxidation of NO_x and deposition of HNO_3 are efficient. Observations of NO_x accumulation in the wintertime troposphere at high latitudes [e.g. Bottenheim et al., 1993; Dickerson et al., 1985; Muthuramu et al., 1994] could be accounted for by formation of stable species such as alkyl nitrates and PANs that have longer lifetimes but are not included in our analysis.

5. Conclusions

In this paper we have used 7 years of measurements at Harvard Forest, 1-2 days downwind of a major source region, to compute the rates for NO_x oxidation and HNO_3 deposition, to determine the reactive-N budget at the site, and to estimate the fraction of N removed in the region near the source. We
found annual average input of 47 mmol m⁻² yr⁻¹, with about twice as much wet as dry deposition. Variations in partitioning between wet and dry deposition tended to offset each other because HNO₃, the main depositing species, is removed efficiently by both processes. Nitrogen deposition at Scheferville was a factor of ~6 less (20 μmol m⁻² d⁻¹ versus. 130 μmol m⁻² d⁻¹) during the summer than the mean summertime rate at Harvard Forest, consistent with a transport time of 2-3 days from emission sources.

Analysis of the regional balance between production and deposition allows us to infer reaction and deposition lifetimes for NOₓ in the boundary layer. The lifetimes for oxidation of NOₓ ranged from 0.24 day in summer, due to the combined effect of homogeneous, heterogeneous, and organic pathways, to 1.4 days in winter, due to heterogeneous processes alone. The lifetimes for deposition of HNO₃ were 1 and 0.6 day in summer and winter, respectively.

Our analysis shows that deposition of reactive N is regulated by the rate of oxidation of NOₓ by reactions with HOₓ radicals, by heterogeneous reactions of N₂O₅, and by organic pathways. Contributions from these three processes are comparable during summer; heterogeneous and organic pathways for NOₓ oxidation are more important than we expected them to be. The presence of forests downwind of source regions enhances rates for nitrogen deposition and increases the fraction of NOₓ retained in the region, because forests are efficient, aerodynamically rough receptors and because biogenic hydrocarbons emitted by vegetation accelerate the rate of oxidation of NOₓ.

The NOₓ emitted from eastern North America is efficiently retained in the region during summer. Export about doubles from summer to winter, but heterogeneous production of HNO₃ is efficient, and ventilation of the boundary layer is relatively slow; hence most of the emitted NOₓ is probably deposited further downwind. Thus remote sites such as Schafferville, 2-3 days' transport from the emission sources, could receive most of their annual reactive-N input during winter when it accumulates in the snowpack and becomes available during spring melt. Only a small fraction of N escapes to the global environment in either season.

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